



US008529825B2

(12) **United States Patent**
Chu et al.

(10) **Patent No.:** **US 8,529,825 B2**
(45) **Date of Patent:** **Sep. 10, 2013**

(54) **FABRICATION OF NANOVOID-IMBEDDED BISMUTH TELLURIDE WITH LOW DIMENSIONAL SYSTEM**

(58) **Field of Classification Search**

USPC 264/614, 620
See application file for complete search history.

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 185 days.

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(21) Appl. No.: **12/928,128**

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(22) Filed: **Dec. 3, 2010**

(57) **ABSTRACT**

(65) **Prior Publication Data**

US 2011/0117690 A1 May 19, 2011

Related U.S. Application Data

(62) Division of application No. 11/831,233, filed on Jul. 31, 2007, now Pat. No. 8,020,805.

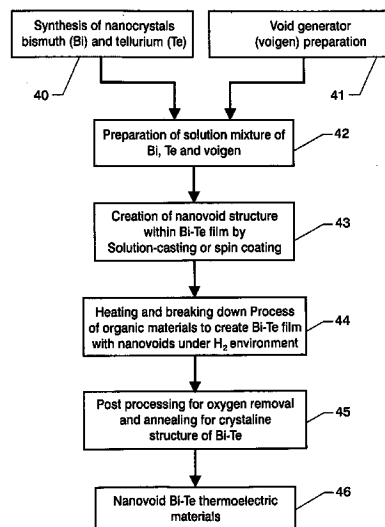
(60) Provisional application No. 60/834,547, filed on Jul. 31, 2006.

(51) **Int. Cl.**
B28B 1/00 (2006.01)

(52) **U.S. Cl.**
USPC **264/620; 264/614**

A new fabrication method for nanovoids-imbedded bismuth telluride (Bi—Te) material with low dimensional (quantum-dots, quantum-wires, or quantum-wells) structure was conceived during the development of advanced thermoelectric (TE) materials. Bismuth telluride is currently the best-known candidate material for solid-state TE cooling devices because it possesses the highest TE figure of merit at room temperature. The innovative process described here allows nanometer-scale voids to be incorporated in Bi—Te material. The final nanovoid structure such as void size, size distribution, void location, etc. can be also controlled under various process conditions.

23 Claims, 22 Drawing Sheets



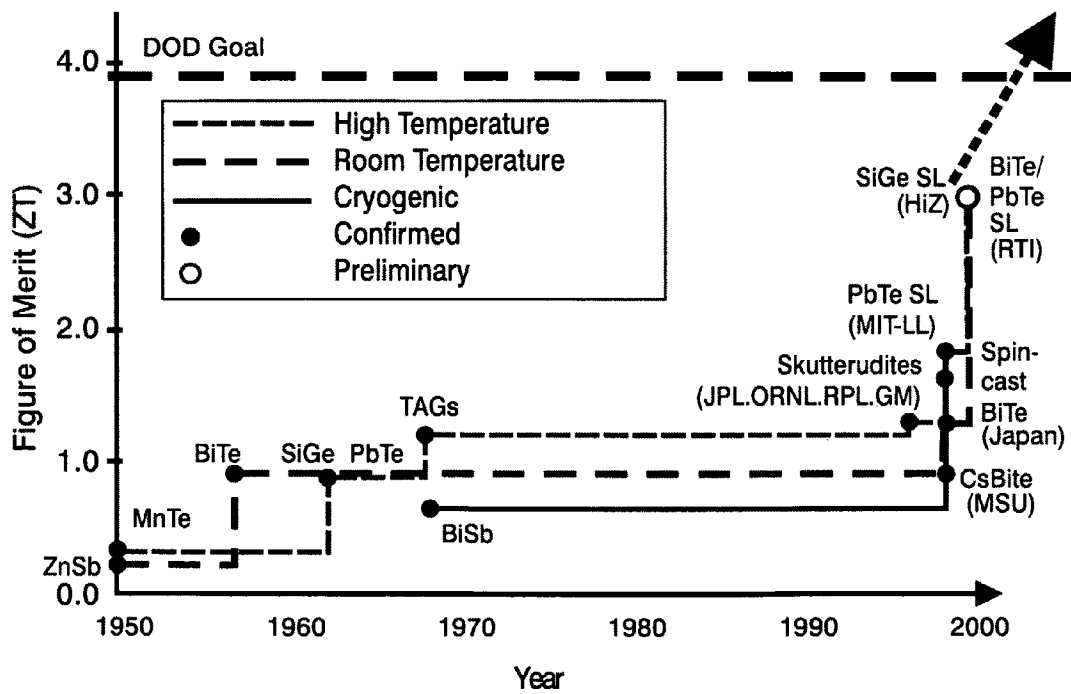


FIG.1

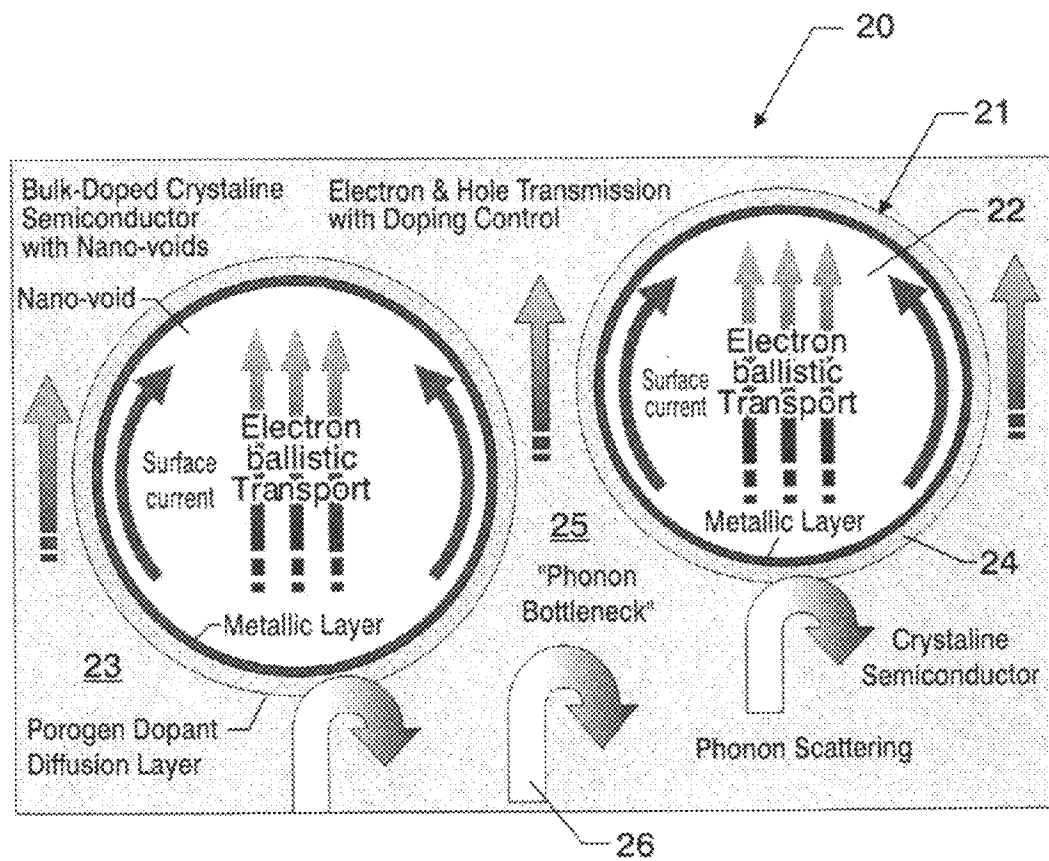


FIG.2

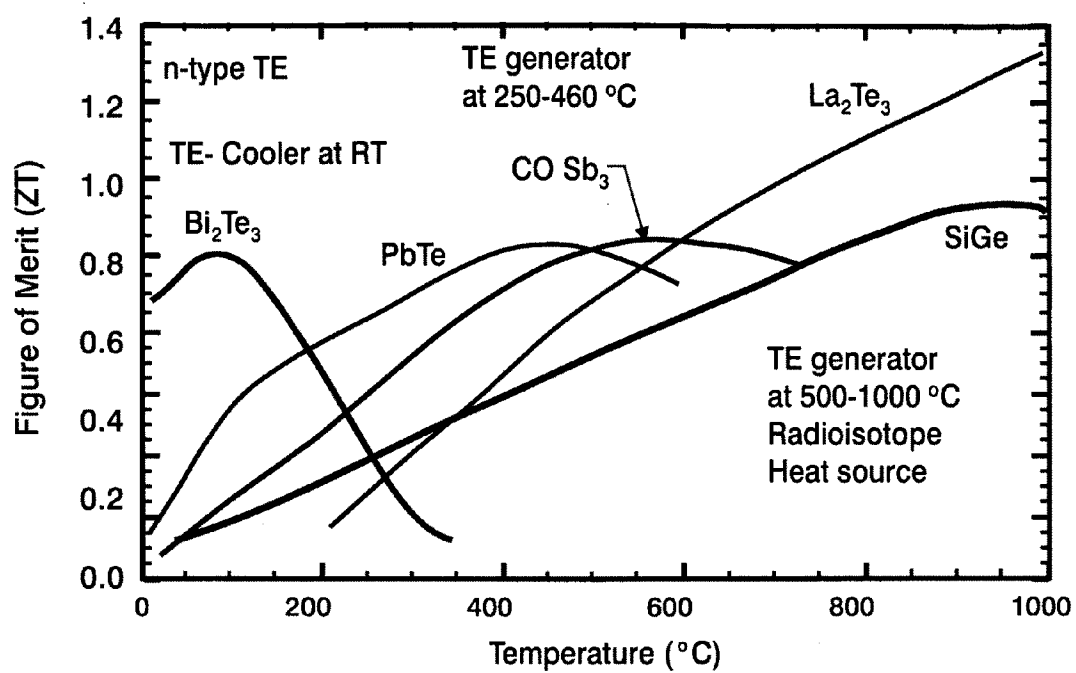
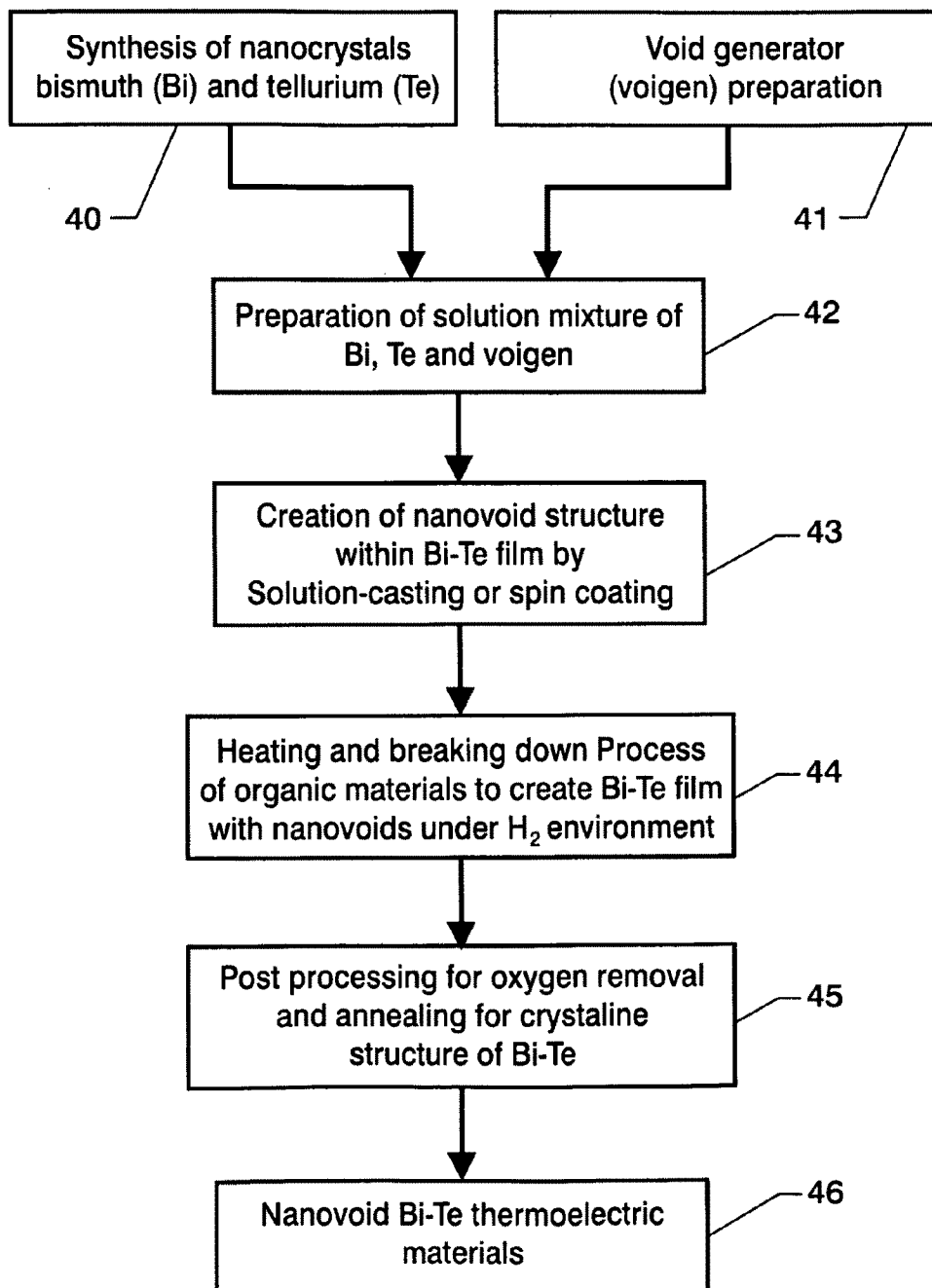


FIG.3

**FIG.4**

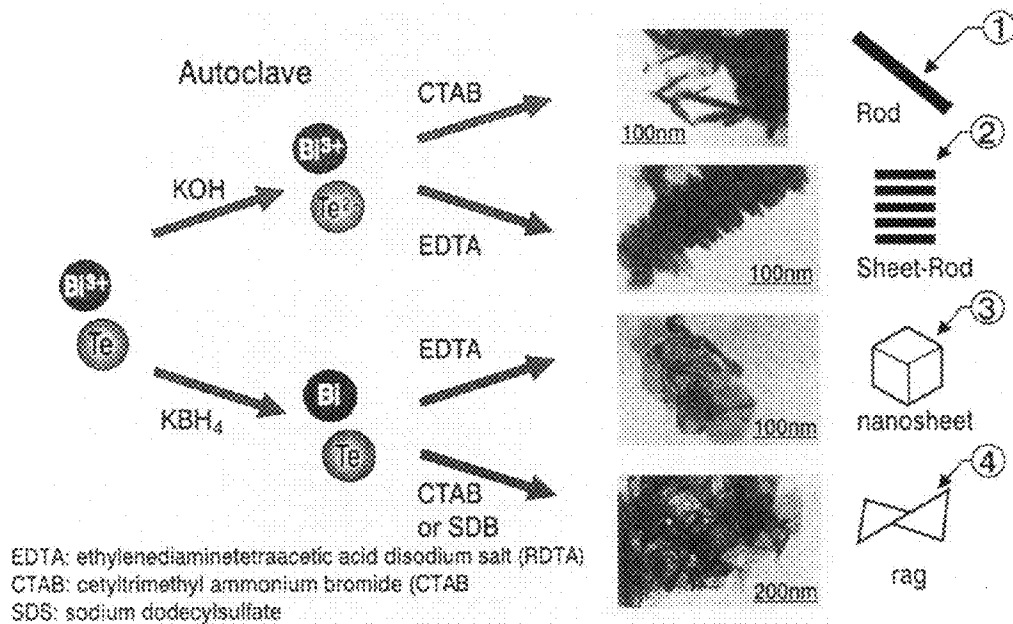


FIG.5

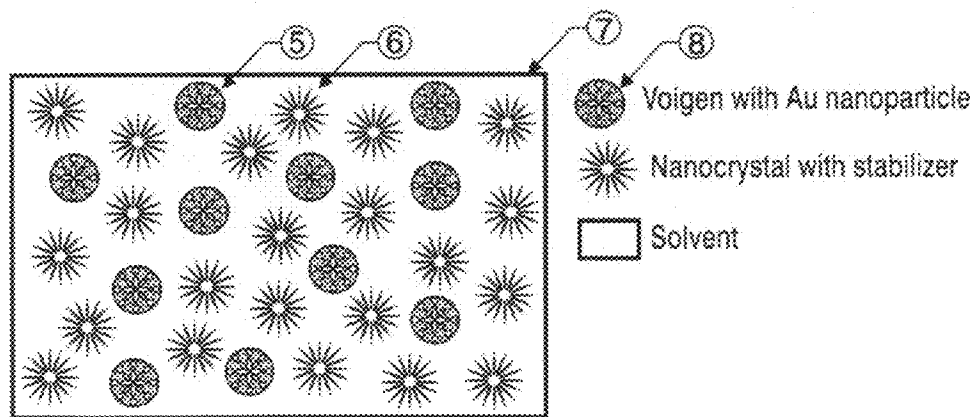


FIG.6

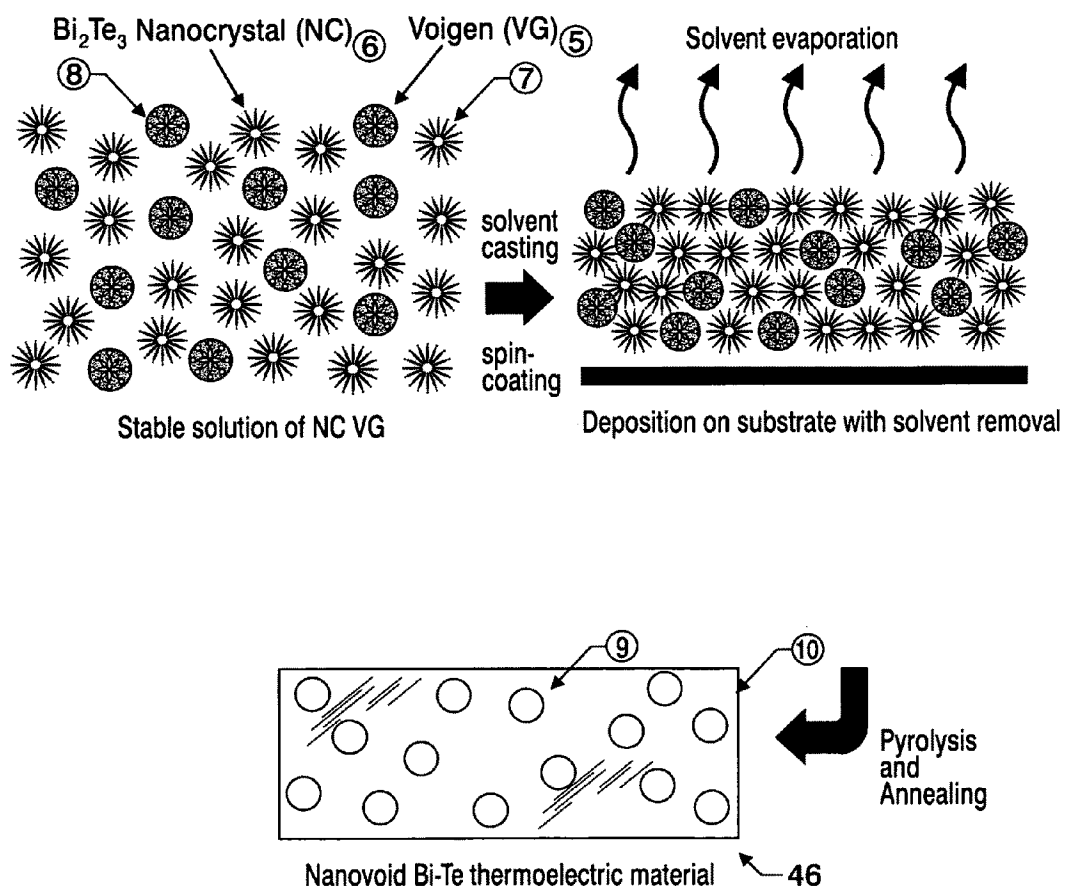


FIG. 7

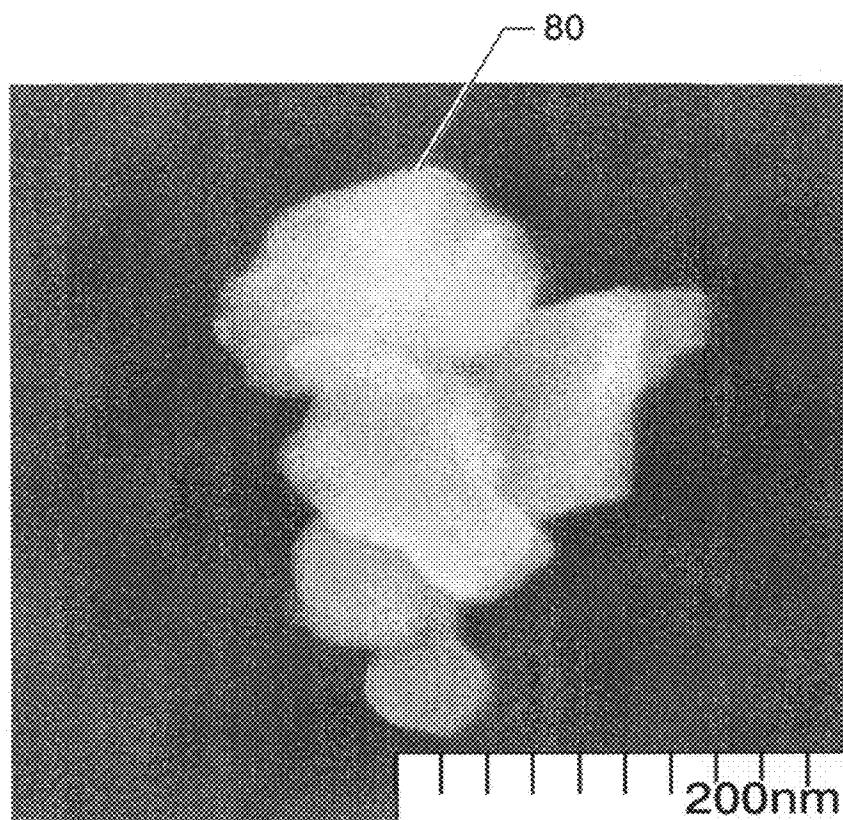


FIG. 8A

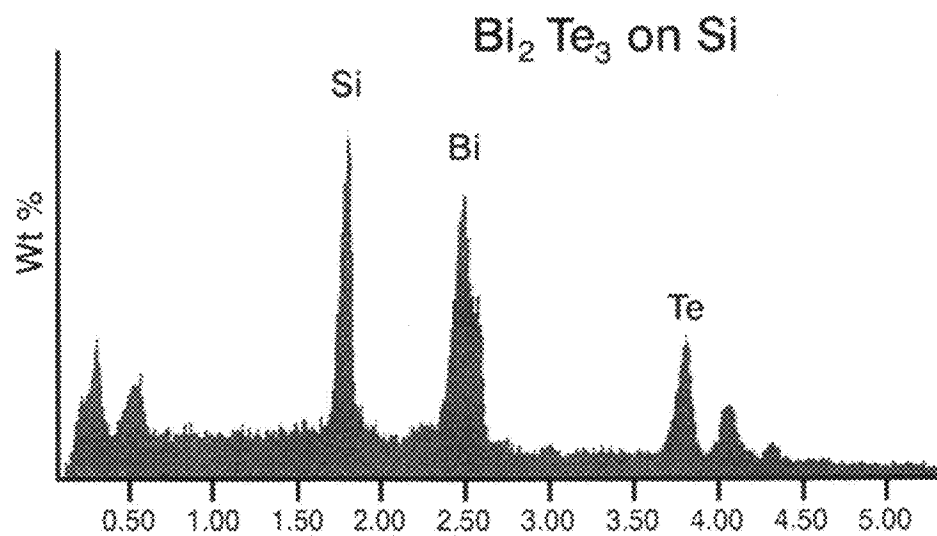


FIG. 8B

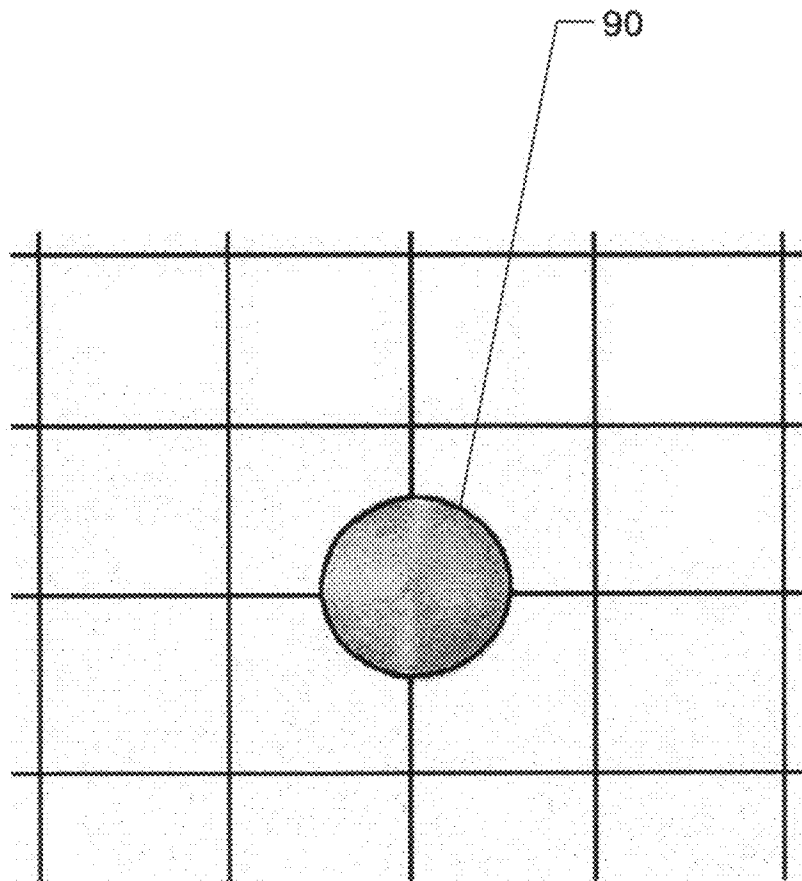


FIG. 9

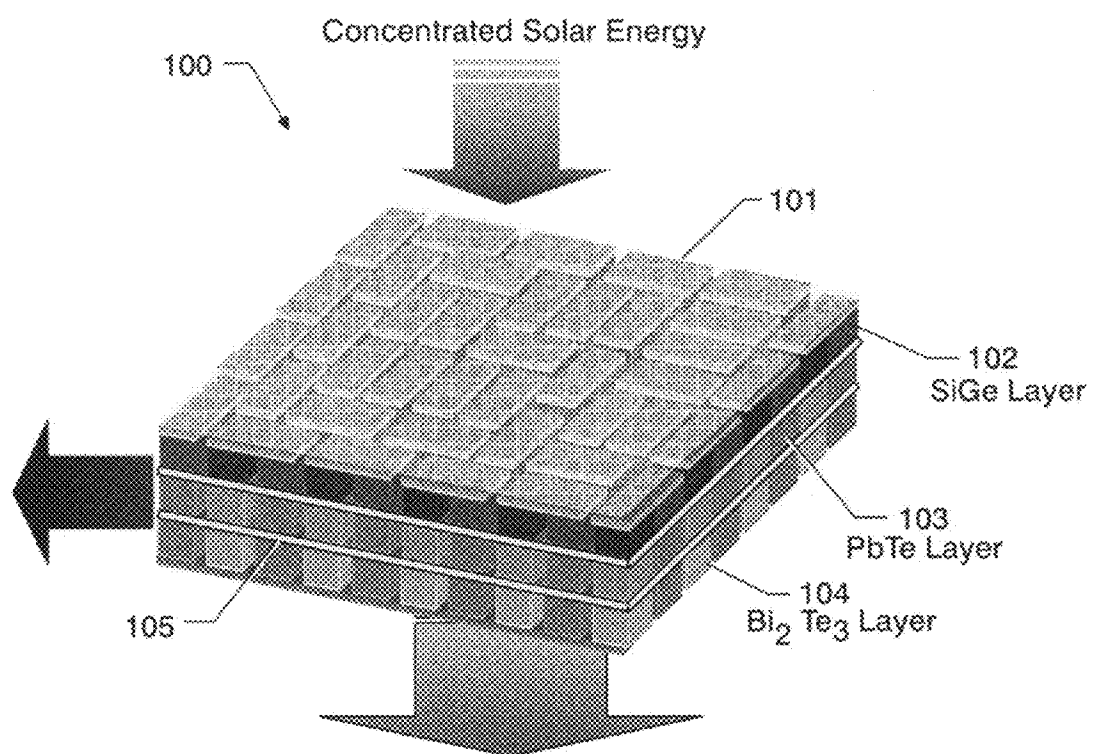


Fig. 10

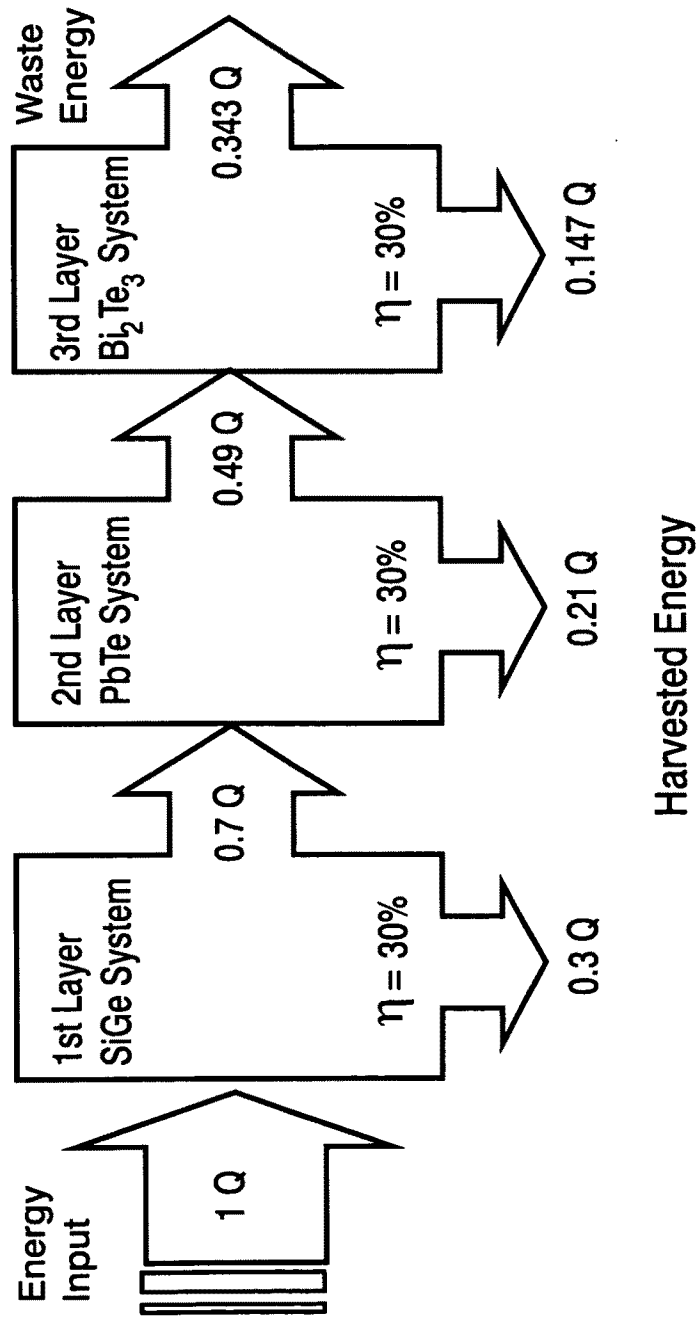


Fig 11

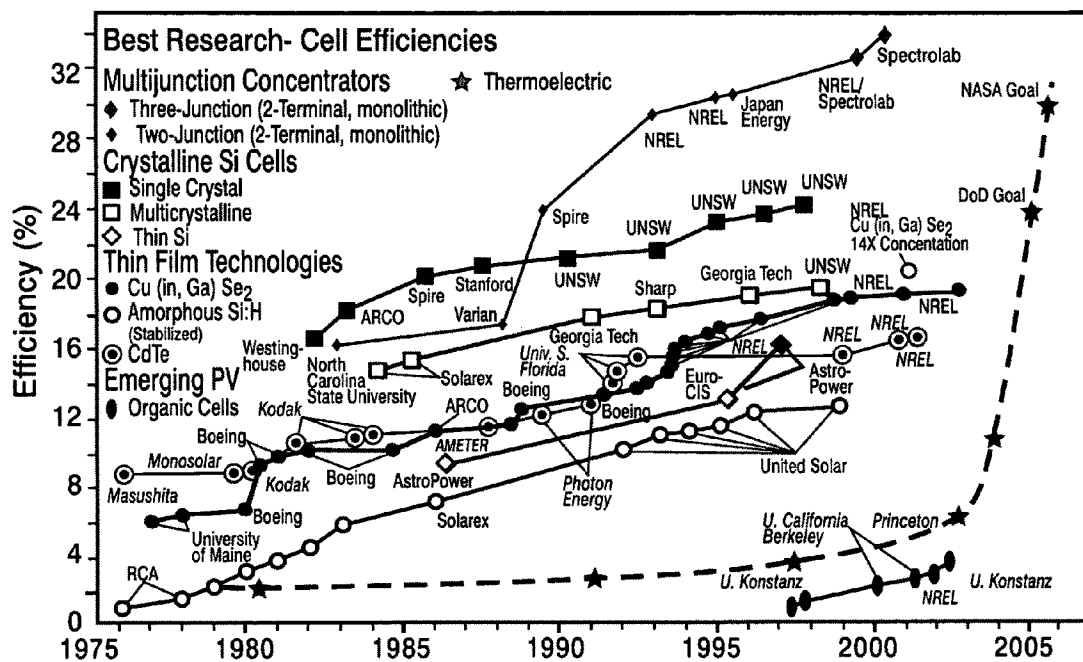


Fig. 12

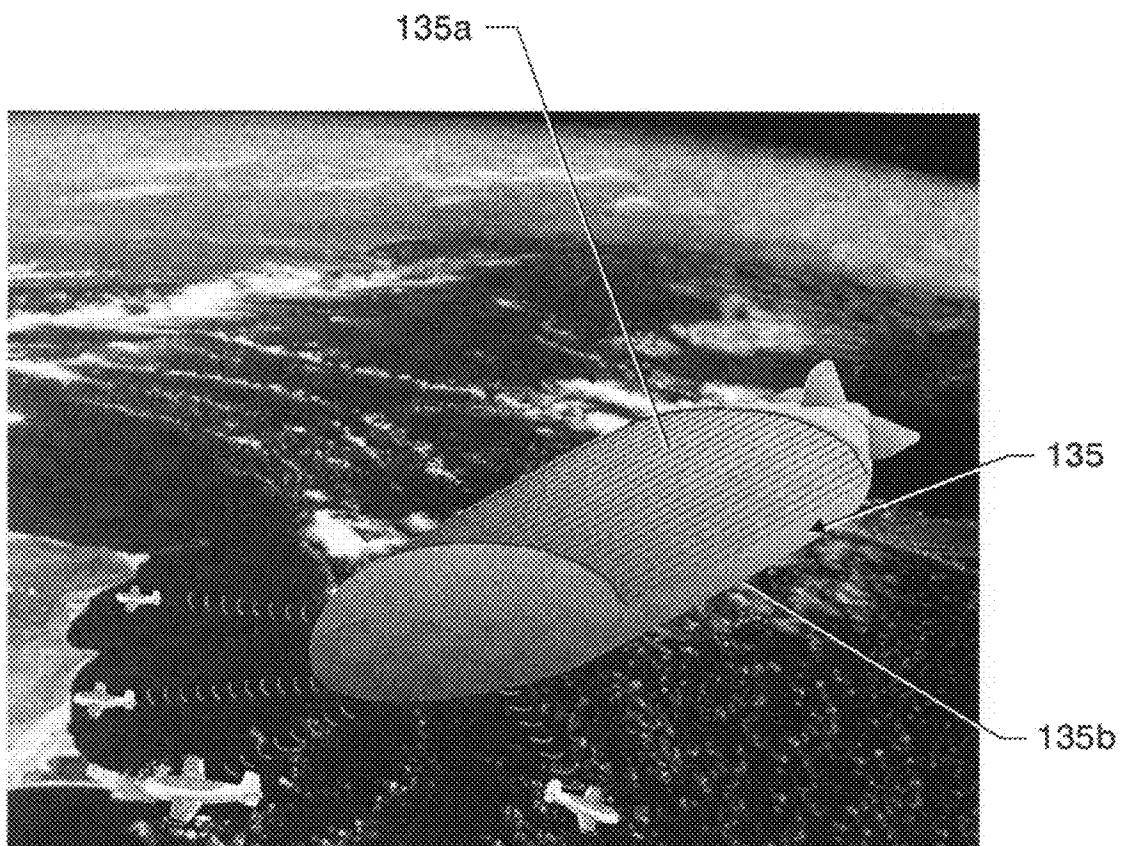


Fig 13A

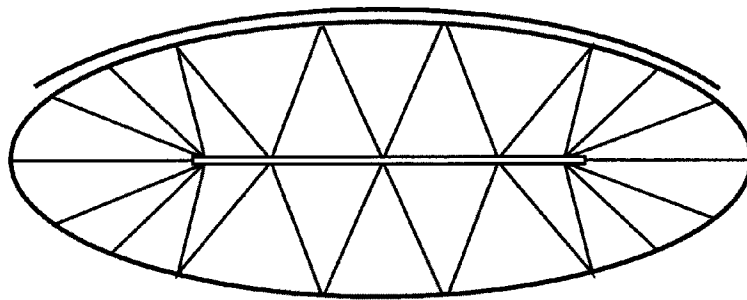


Fig 13B

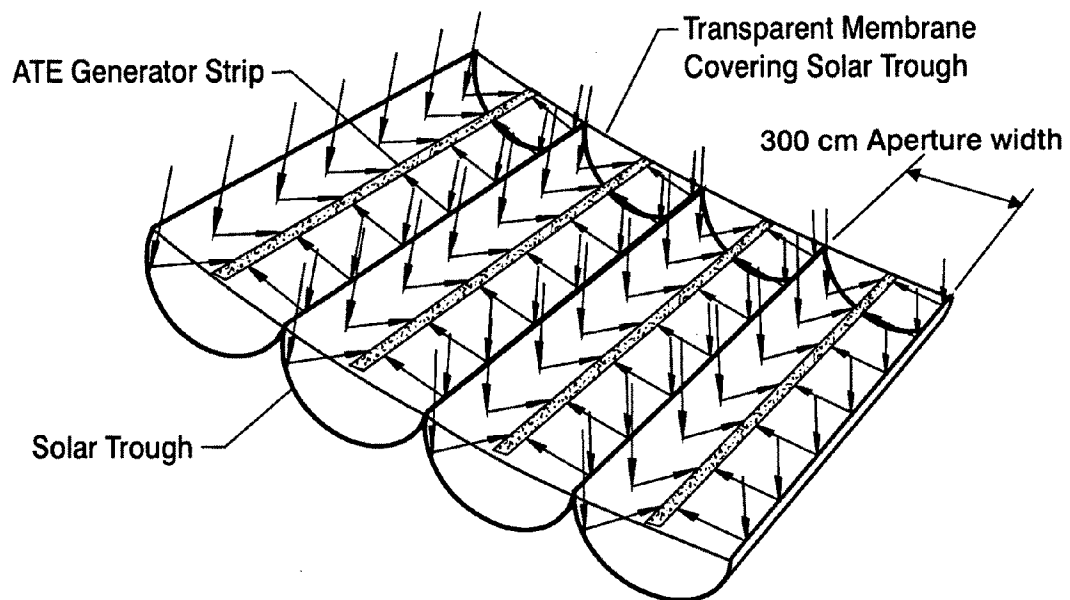


Fig 13C

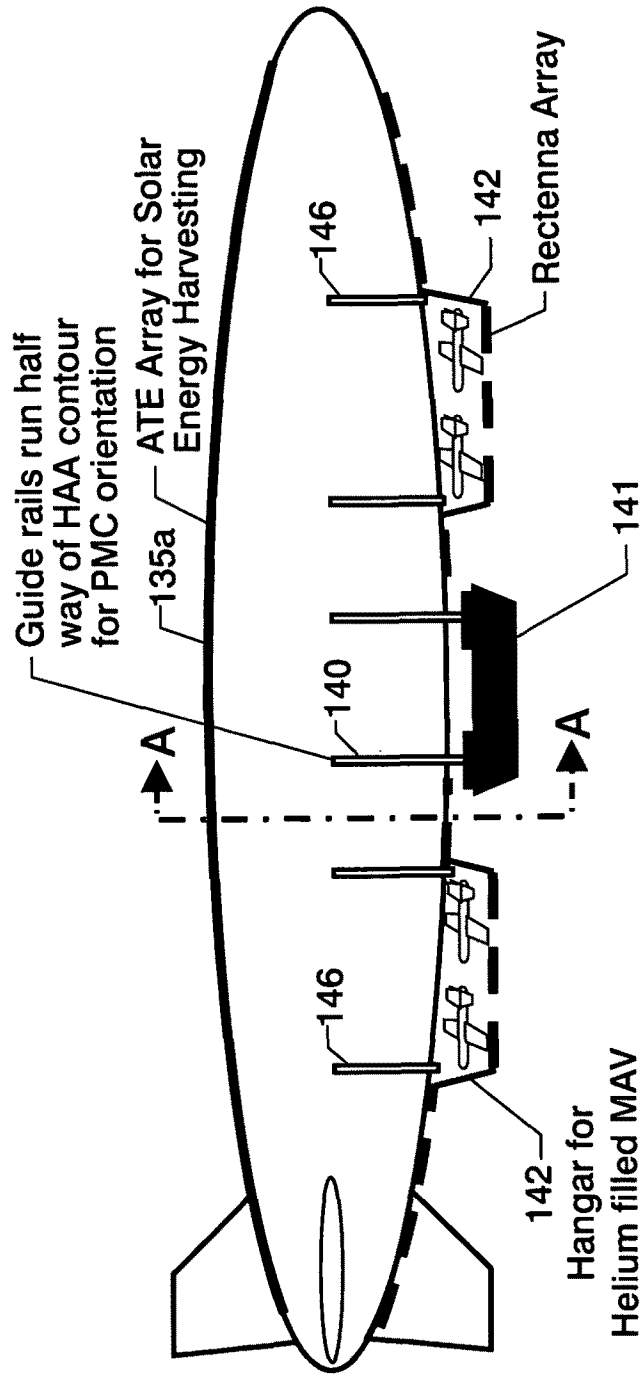


Fig 14

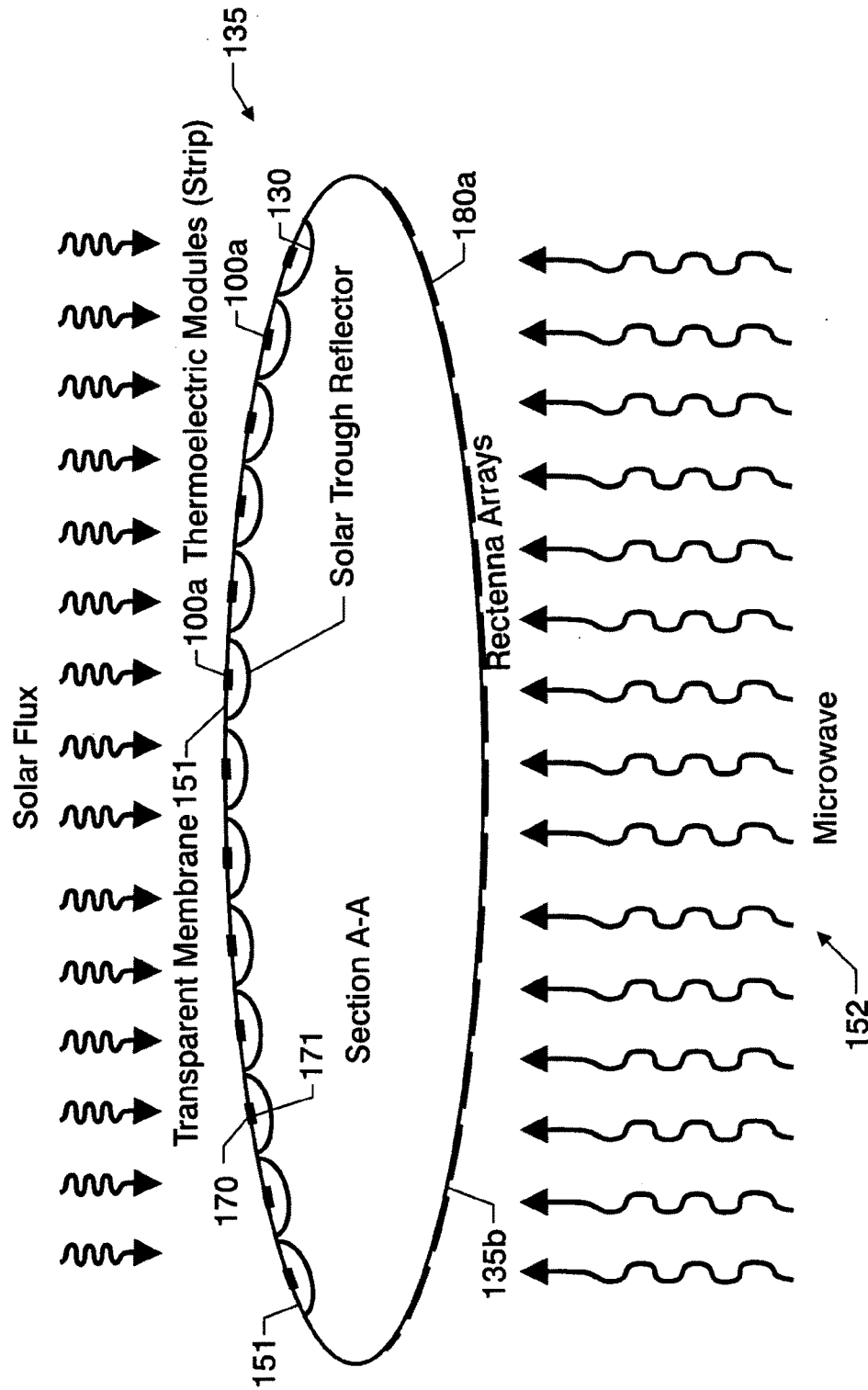


Fig 15

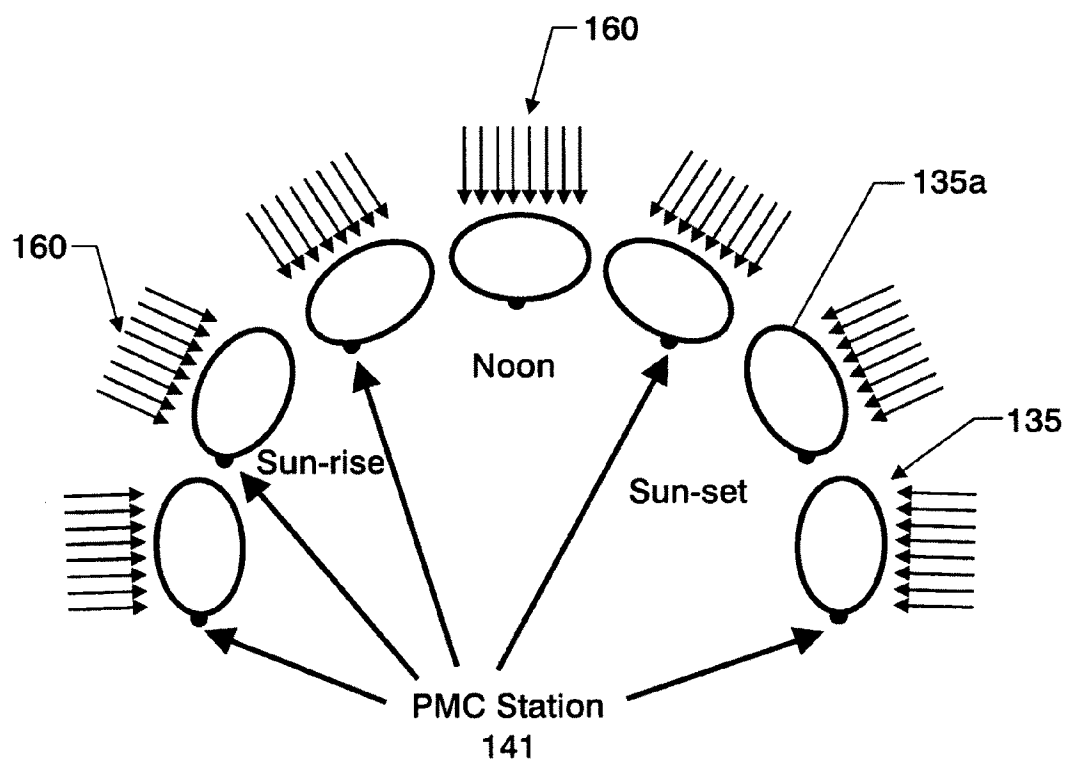


Fig 16

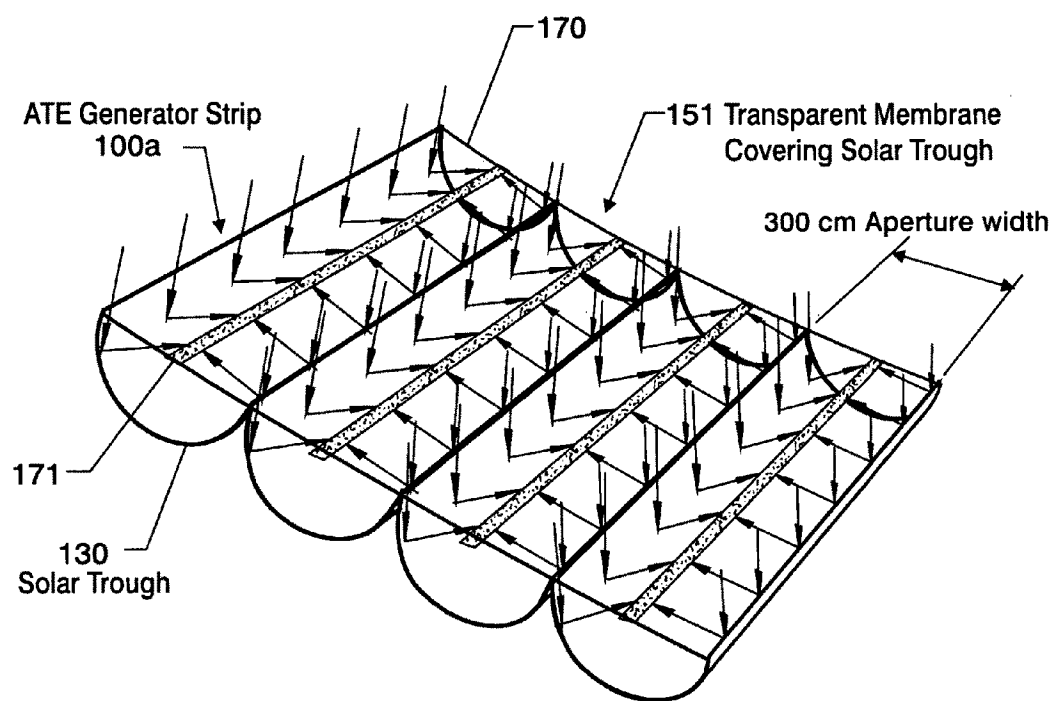


Fig. 17

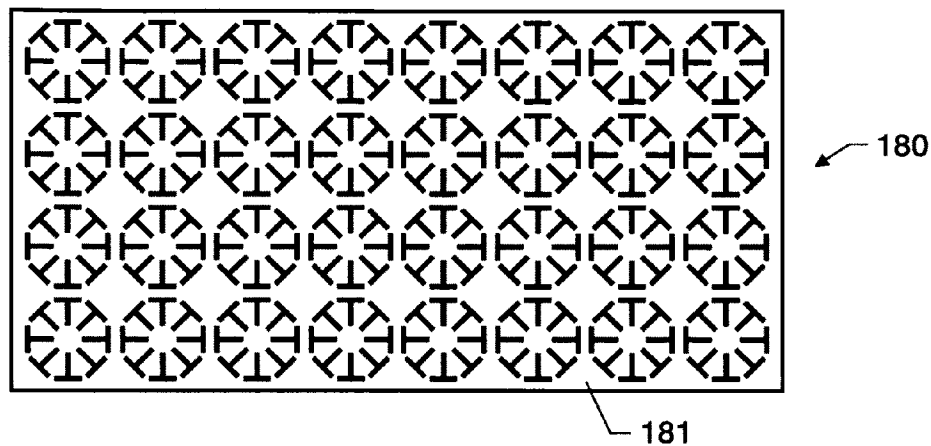


Fig. 18A

Circuit of Thin-Film Rectenna Dipole Element

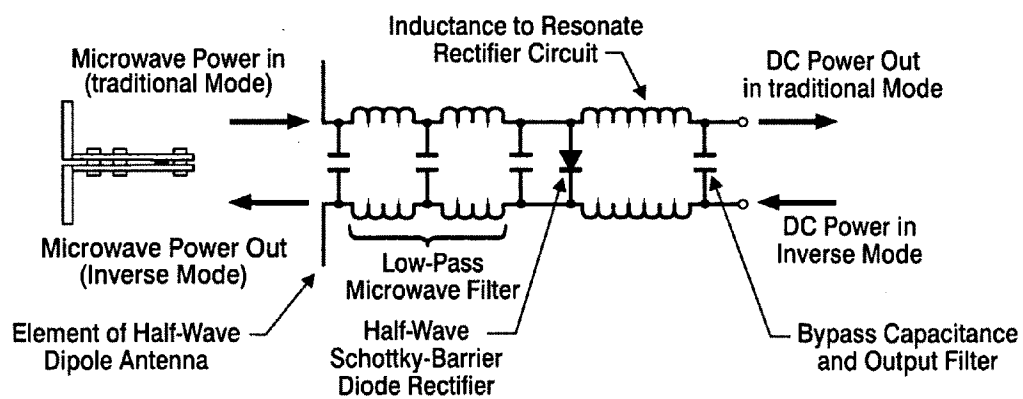


Fig. 18B

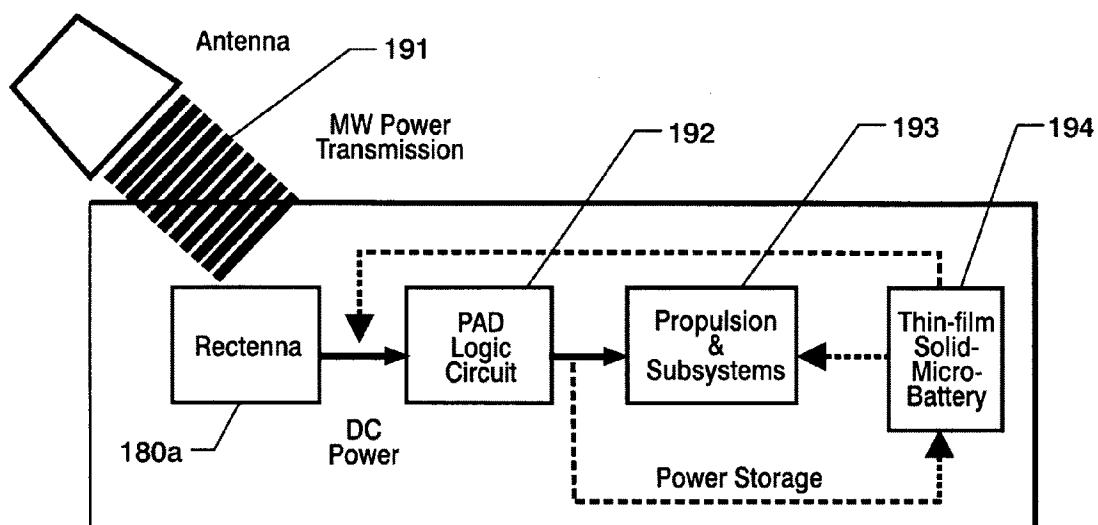


Fig. 19

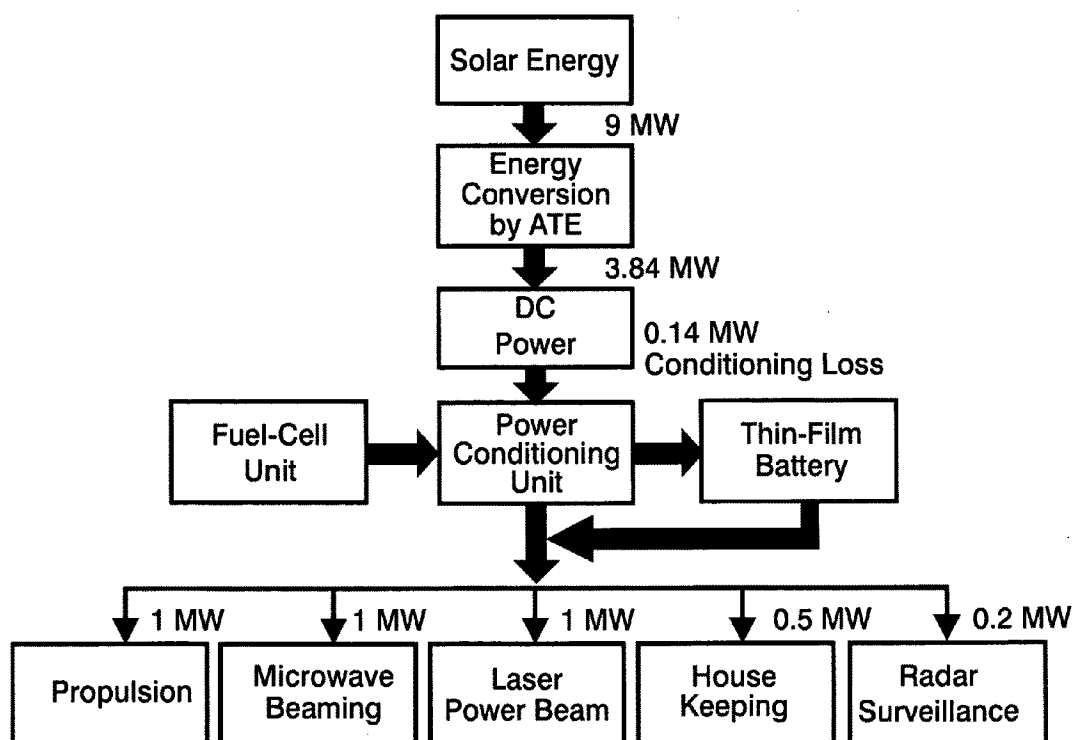


Fig. 20

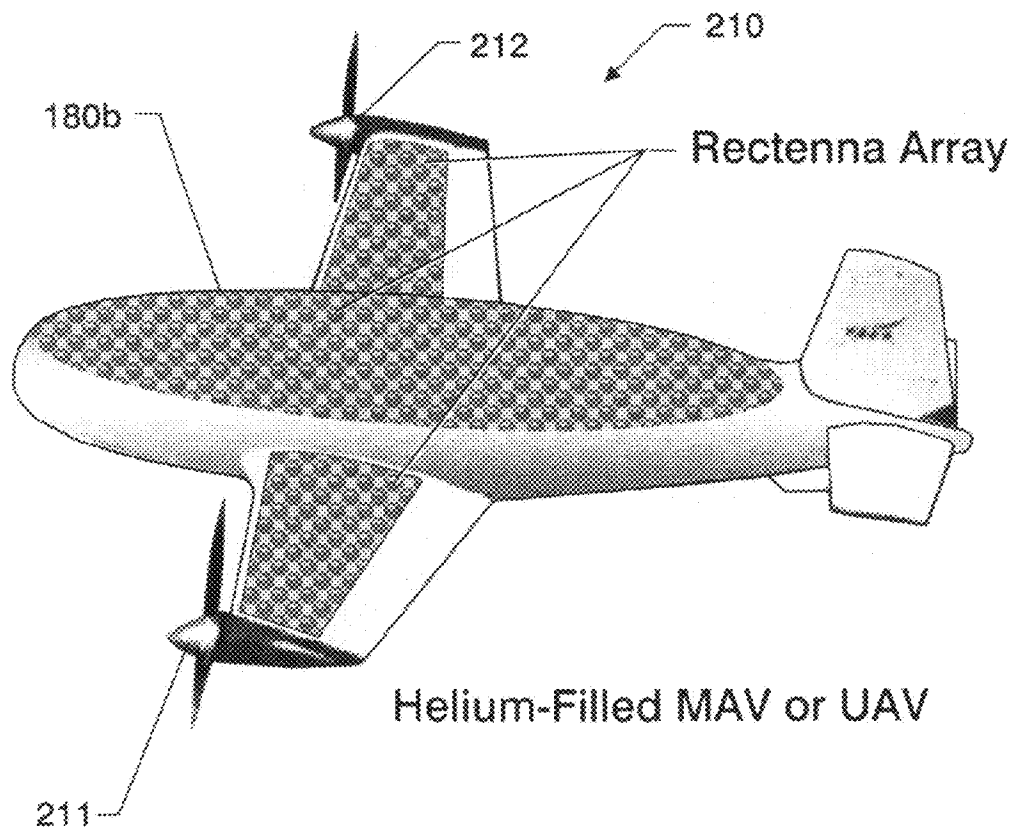


Fig. 21

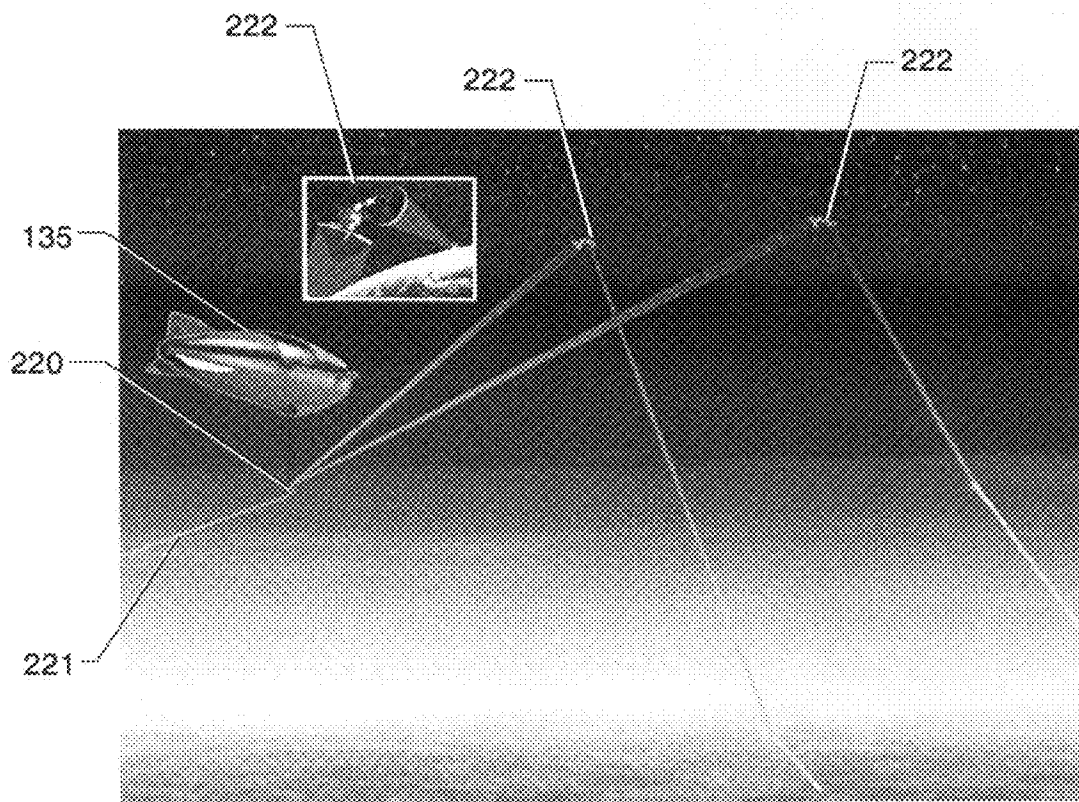


Fig. 22

FABRICATION OF NANOVOID-IMBEDDED BISMUTH TELLURIDE WITH LOW DIMENSIONAL SYSTEM

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Divisional application of prior pending U.S. patent application Ser. No. 11/831,233 filed Jul. 31, 2007 now U.S. Pat. No. 8,020,805 and published Mar. 19, 2009 as U.S. 2009/0072078, which claims the benefit of U.S. provisional application 60/834,547, with a filing date of Jul. 31, 2006. The entire disclosure of the prior application is hereby incorporated by reference herein in its entirety. This invention was made in part by employees of the United States Government and may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms, as provided for by the terms of Contract No. NCC-1-02043 awarded by the National Aeronautics and Space Administration, and Science and Technology Corporation Contract Nos. L-71200D and L-71407D.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention generally relates to a fabrication method for a thermoelectric material. More specifically, the invention relates to a fabrication method for a nanovoid-imbedded bismuth telluride with a high figure of merit.

2. Description of the Related Art

To date, void-incorporated thermoelectric (TE) materials have been studied in only a few compound systems, such as bismuth, silicon, Si—Ge solid solutions, Al-doped SiC, strontium oxide and strontium carbonate. Si—Ge samples prepared by Pulverized and Intermixed Elements Sintering (PIES) method exhibited 30% increase in TE performance with 15-20% void fraction. Based on recent experimental research, theoretical calculations also indicated that it is possible to increase the ZT of certain materials by a factor of several times their bulk values by preparing them in 1D or 2D nanostructures. Bi—Te materials, especially with low-dimensional system, have been fabricated through solvo-thermal method (1D or 2D nanocrystals), metal-organic chemical vapor deposition (MOCVD) (2D superlattice structure), electrodeposition in porous alumina substrates (1D nanowire), and reverse micelle method (0-D quantum dots).

Typical void sizes in most of prior-art studies were in the micrometer range and no appreciable reduction in thermal conductivity was realized. Lower thermal conductivity contributes to the thermoelectric performance and in the prior-art studies, no noticeable phonon disruption was observed. Aside from theoretical predictions, there are no TE materials, based on Bi—Te, that have demonstrated such an enhancement in ZT values due to low-dimensional crystalline system. The previous studies also showed most of voids in Bi—Te film existed in an interconnected form which causes poor electron

mobility, resulting in lower electrical conductivity and hence, lower thermoelectric performance.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a fabrication method for a thermoelectric material.

Another object of the present invention is to provide a fabrication method for a thermoelectric material having a high figure of merit.

Another object of the present invention is to provide a fabrication method for a thermoelectric material having increased electrical conductivity.

Another object of the present invention is to provide a fabrication method for a thermoelectric material having reduced thermal conductivity.

Another object of the present invention is to provide a fabrication method for nanovoid-imbedded bismuth telluride with low dimensional system.

Another object of the present invention is to provide a fabrication method for nanovoid-imbedded bismuth telluride with a high figure of merit.

Other objects and advantages of the present invention will become more obvious hereinafter in the specification and drawings.

In accordance with the present invention, a method for forming high figure of merit thermoelectric materials is disclosed. The method includes providing nanocrystals of bismuth and tellurium and preparing a void generator material including a plurality of nanoparticles each having a metallic outer coating. The void generator material is preferably an organic material and more preferably a ferritin protein. A solution mixture of the bismuth nanocrystals, tellurium nanocrystals and the void generator material is prepared and deposited onto a substrate, preferably silicon. The deposition method may be spin-coating, dipping, or solvent casting or any other appropriate method. The deposited solution mixture is heated in an oxygen environment to create a plurality of nanovoid structures from the nanoparticles to provide a nanovoid incorporated bismuth-tellurium film. In the preferred method, the deposited solution mixture is heated to no more than 400° C. for approximately one hour in an oxygen environment which is 99.999% pure oxygen. Following the heating, the film is treated to remove any oxygen components remaining from heating the mixture in the oxygen environment and to cause the formation of a crystalline structure in the film. Such treatment is preferably accomplished by hydrogen calcination and hydrogen plasma quenching.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention, including other objects and advantages, reference should be made to the Detailed Description of the Invention set forth below. This Detailed Description should be read together with the accompanying drawings, wherein:

FIG. 1 is a graph depicting the History of Thermoelectric Figure of Merit (ZT);

FIG. 2 is an illustration of a morphological design of an advanced thermoelectric material to enhance the ZT by increasing electrical conductivity while concurrently reducing thermal conductivity by populating nanovoids into the material, which material can be utilized in at least one embodiment of the present invention;

FIG. 3 is a graph of the figure of merit of several TE materials which could be utilized in at least one embodiment of the present invention;

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FIG. 4 is a flow chart of the fabrication of a nanovoid bismuth telluride (Bi—Te) thermoelectric material that could be utilized in at least one embodiment of the present invention;

FIG. 5 is a diagram depicting a portion of the fabrication process of the Bi—Te thermoelectric material referenced in FIG. 4, i.e., the formation of low-dimensional bismuth telluride nanocrystals using solvo-thermal process;

FIG. 6 is a diagram depicting a portion of the fabrication process of the Bi—Te thermoelectric material referenced in FIG. 4, i.e., a three-phase mixture of Bi—Te NCs, voids, and cosolvent;

FIG. 7 is diagram depicting a portion of the fabrication process of the Bi—Te thermoelectric material referenced in FIG. 4, i.e., fabrication of nanovoid Bi—Te material by deposition and pyrolysis process that creates nanovoid structure in thermoelectric material;

FIG. 8A is an image of two-dimension nanosheets fabricated using bismuth telluride crystals which can be utilized in at least one embodiment of the present invention;

FIG. 8B is a graph of element analysis data by EDAX of same the nanosheets shown in FIG. 8A;

FIG. 9 is an image of a bismuth telluride disk fabricated by a cold press method, which can be utilized in at least one embodiment of the present invention;

FIG. 10 is a perspective view of one possible embodiment of the Advanced Thermoelectric (ATE) energy conversion system of the present invention;

FIG. 11 is a flow chart depicting the cascaded efficiency of a 3-layer ATE system in a tandem mode in accordance with at least one embodiment of the present invention;

FIG. 12 is a graph depicting the efficiencies of state-of-the-art solar, and thermoelectric cells;

FIG. 13A is a perspective view of a flattened airship with ellipsoidal cross-section to maximize the reception of solar flux in accordance with at least one embodiment of the present invention;

FIG. 13B depicts the ellipsoidal cross section of the airship shown in FIG. 13A;

FIG. 13C is an expanded view of the solar troughs disposed on the top surface of the airship shown in FIG. 13A, utilizing the ATE conversion system;

FIG. 14 is a side-view drawing of another embodiment of an HAA of the present invention;

FIG. 15 is the cross-sectional view of the HAA along the plane indicated by dashed line A-A in FIG. 14;

FIG. 16 are front views of an HAA, depicting a method of operation of the HAA, in accordance with at least one embodiment of the present invention;

FIG. 17 is a drawing of the troughs shown in FIG. 13C, depicting ATE power modules utilized with linear parabolic troughs to collect solar flux, in accordance with at least one embodiment of the present invention;

FIG. 18A is a drawing of a flexible thin-film rectenna array that, in at least one embodiment of the present invention, can be attached under the bottom surface of an HAA to receive and convert microwave power into DC Power;

FIG. 18B illustrates an example of a circuit that could be utilized in the rectennas depicted in FIG. 18A;

FIG. 19 is a logic diagram of potential microwave power use by an HAA equipped with a rectenna array, such as the array depicted in FIG. 18;

FIG. 20 is flow chart depicting a possible power distribution scenario of an HAA for various application devices that might be onboard;

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FIG. 21 is a perspective view of a novel unmanned or manned aerial (UAV or MAV) configured for electric propulsion power to be wirelessly transmitted; and

FIG. 22 is an image depicting an HAA utilizing a sophisticated relay system of laser power.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises incorporation of controllable nanovoid structures into bismuth telluride (Bi—Te) thermoelectric materials using Bi—Te nanocrystal process, in order to achieve high figure of merit for TE devices. One advantageous embodiment of the present inventive system, or device, is based on advanced thermoelectric (ATE) materials which can be developed for a targeted figure of merit (FoM) goal, advantageously, greater than 5. This inventive power technology enables many application specific scenarios which might not have been possible with prior technology.

As shown in FIG. 1, the FoMs of most TE materials developed to date are still below 2. A FoM of 1 is equivalent to a thermal to electrical energy conversion efficiency greater than 6%. To achieve advanced TE (ATE) materials 20 with a high FoM, nanovoids 21 can be incorporated, as shown in FIG. 2, into the TE materials 23 to increase the electrical conductivity (EC) while reducing the thermal conductivity (TC). The nanovoids 21 are essentially nano spherical shells 24 having internal voids 22. In one embodiment, spherical shells 24 of approximately 10 nm to approximately 20 nm in outer diameter can be made from a metallic component such as gold or cobalt using a bio-template, as discussed in more detail below. The void 22 inner diameter can range from approximately 10 nm to approximately 12 nm. The void diameter needs to be small enough to avoid a reduction in electrical conductivity and a change in morphology of the bulk material to poly-crystalline.

Typically, within a crystalline structure of a material, the heat transfer mechanism is mainly dictated by phonon transmission (>70%) rather than by energetic electrons (<30%) for temperatures below 900 K. Accordingly, a method to manipulate the phonon transmission within a crystalline medium offers a capability to control the thermal conductivity. The metallic nanovoids 21 populated inside bulk matrix TE materials 23 create large phonon scattering cross-sections that effectively block the transfer of thermal energy through them. The TE material 23 in an unoccupied area 25 that is sandwiched between nanovoids 21 will become a phonon 26 bottleneck since the narrowly sandwiched bulk material is under a high tension induced from the spherical formation of the TE material boundary around the nanovoids, as shown in FIG. 2. The phonon bottleneck is essentially the combination of unoccupied area 25 and the nanovoids 21. The individual phonon 26 merely indicates that the phonon 26 cannot propagate easily through the unoccupied area 25. The structure of the TE material boundary surface around the spherical nanovoids 21 may be framed of a high energy bonding group that develops high tension over the surface. The material structure with high tension would be less subjected to an oscillatory mode transmission than material structures in normal tension. Therefore, both the high tension and the narrow passage 25 between nanovoids are resistive to phonon transmission and accordingly regarded as a phonon bottleneck. Ultimately, the imbedded nanovoids 21 create the phonon scattering cross-sections and bottlenecks throughout the matrix material as shown in FIG. 2.

The selection basis of TE materials for the present invention can be according to the temperature at which the performance of the particular TE material is best-suited. For

example, in at least one advantageous embodiment of the present invention, the materials selected can be silicon-germanium (SiGe) and bismuth telluride (Bi_2Te_3), along with lead telluride (PbTe). Currently pending U.S. patent application Ser. No. 11/242,415, entitled "Silicon Germanium Semiconductive Alloy and Method of Fabricating Same, by Park, et al., filed on Sep. 27, 2005, and hereby incorporated by reference as if set forth in its entirety herein, discloses additional detail relative to a lattice-matched silicon germanium semiconductive alloy and its fabrication that is suitable for use in at least one layer of the present invention. Materials desirable for use would also include nanovoid-imbedded forms of Si Ge, PbTe, and Bi_2Te_3 .

Nanovoid-imbedded Bi—Te would be suitable for use in one or more different layers. Bismuth Telluride is currently used in solid-state TE cooling devices due to its high figure of merit at room temperature, as shown in FIG. 3, but its applications are still limited by poor TE properties. To improve TE performance, nanometer-scale voids can be incorporated into Bi—Te material, with the void size, size distribution, void location, etc. controlled under various process conditions. The nanovoids reduce thermal conductivity by disrupting phonons without sacrificing electron transport, thereby allowing for the reduction of thermal conductivity while increasing electrical conductivity. The nanovoid incorporation is controlled by thermodynamic miscibility and kinetic mobility of two phases, TE precursor and voigen. Metal nanoparticles such as but not limited to gold, cobalt, platinum, manganese, and iron, anchored on the voigen material surface eventually form a metal layer or lining through an annealing process. The spherical void by metal lining becomes a passage of mobile electrons and aids the electrons to move through the nanovoid structure.

There are several methods for imbedding nanovoids into a matrix material. For example, in the solvo-thermal method which can be used for Bi_2Te_3 , the nanocrystals of bismuth telluride are created and then mixed with nanovoids before solvent casting. Through solvent casting on a substrate after mixing, a cake of bismuth telluride is made. This cake goes through calcination and hydrogen plasma etching processes to remove unwanted impurity elements. Finally, the sponge form of bismuth telluride is sintered to become a matrix of single crystal deposition.

To date, the void-incorporated TE materials have been studied in several compound systems, such as bismuth, silicon, Si—Ge solid solutions, Al-doped SiC, strontium oxide and strontium carbonate. Si—Ge samples prepared by Pulverized and Intermixed Elements Sintering (PIES) method exhibited 30% increase in TE performance with 15-20% void fraction. Theoretical calculations also indicate that it is possible to increase the ZT of certain materials by a factor of several times their bulk values by preparing them in 1D or 2D nanostructures. Bi—Te materials, especially with low-dimensional system, have been fabricated through solvo-thermal method (1D or 2D nanocrystals), metal-organic chemical vapor deposition (MOCVD) (2D superlattice structure), electrodeposition in porous alumina substrates (1D nanowire), and reverse micelle method (0-D quantum dots).

Nanovoids are incorporated, in a controllable manner, into bismuth telluride (Bi—Te) thermoelectric materials using a Bi—Te nanocrystal process, in order to achieve a high figure of merit. The fabrication process is shown in FIG. 4. An important element in developing high figure of merit TE materials is to fabricate void generators ("voigens") and to populate voigens into the bulk TE materials. The population distribution of voigens into bulk TE materials determines the reduction level of thermal conductivity by setting up phonon

bottlenecks between voigens where phonon scattering takes place. As such, the population density will depend on the desired thermal conductivity.

First, precursor materials are prepared for syntheses of Bi—Te nanocrystals 40. Various Bi—Te nanocrystals can be prepared by employing the solvo-thermal process. Nanocrystals of various sizes and shapes can be made by changing synthesis conditions, as illustrated in FIG. 5. Possible geometries of nanocrystals include nanorod, nanosheet, nanosheet-rod, nanorag, etc.

Another important part of material preparation is to synthesize voigen materials 41. Voigen materials are designed to meet several important roles for high figure of merit TE materials: (1) phonon scattering centers, (2) reduced thermal conductivity, and (3) enhanced electrical conductivity. Creation of nanovoids with size and shape uniformity is also an important issue that will determine void fraction within bulk TE materials. To enhance electrical conductivity, voigen materials (e.g., ferritin protein), which are in a nano-scale, generally approximately 8 nm inner diameter and 12 nm outer diameter are coated with a metal lining, such as but not limited to gold, cobalt, platinum, manganese, and iron. While the voigen material is not limited to ferritin protein and may be other bio-templates, the ferritin protein is generally desirable due to its ability to form the spherical shape with void. The metal nanoparticles anchored on the voigen material surface eventually form a metal layer or lining through an annealing process. The annealing process comprises hydrogen calcination and hydrogen plasma quenching. The metal lining is approximately several atomic layer thick and generally no more than approximately 3 to 4 nanometers. Nanometer-scaled voigen molecules can be dispersed in a cosolvent system with Bi—Te nanocrystals 42, as illustrated in FIG. 6. The nanoscale phase separation between the precursor and voigen is induced by their thermodynamic miscibility, and determines the final nanovoid structure. The diameter of voigen materials is designed to be less than approximately 20 nm after coated with the metal nanoparticles. The metal nanoparticles will remain as a metal lining that forms a spherical void after a pyrolysis process. The metal lining that forms the spherical void forms the passage for electrons which provides for high electrical conductivity. In conjunction with the reduced thermal conductivity attributed to the phonon scattering of nanovoids, the enhancement of electrical conductivity is desirable for high figure of merit TE performance. Overall TE performance can be possibly deteriorated by the aggregation of metallic spherical voids without spreading within the bulk material. Accordingly, the distribution of nanovoids throughout the TE material is important.

The mixture of the three-phase system (bismuth, tellurium, and voigens) is deposited on a substrate using solution-based thin-film coating methods. Known substrates, such as silicon, are suitable. Suitable coating methods include spin-coating, dipping, solvent casting, etc. 43. After coating or casting, the films are placed in a vacuum chamber and heated under the environment of ultra pure hydrogen (approximately 99.999%) 44. A temperature of less than approximately 400° C. is generally desirable. The heating time is dependent on the thickness of the film, but generally approximately one hour. Voigen material which is organic, such as ferritin protein, and other organic components from the solution used are thermally decomposed and removed during pyrolysis process 44 until nanovoid-incorporated Bi—Te film 46 is obtained, as illustrated in FIG. 7. Hydrogen calcination and hydrogen plasma quenching 45 are then used, which first remove oxygen components that are the residue of organic breakdown

with hydrogen plasma and second make crystalline structure in Bi—Te films through the annealing process, respectively.

A solvothermal pre-process to make the Bi_2Te_3 nanoparticles successfully produced black powder of bismuth telluride crystal with low dimension. FIG. 8A shows two-dimensional nanosheets **80** fabricated using potassium hydroxide (KOH) and ethylenediamine tetraacetic acid (EDTA), following the synthesis process described in FIG. 5. The nanosheets varied in size, all thicker than approximately 30 nm, and Energy dispersive X-ray spectroscopy (EDAX) analysis using FE-SEM (Field Emission Scanning Electron Microscopy) confirmed the existence of Bi_2Te_3 by element energy analysis, as shown in FIG. 8B. The thickness of the nanosheet is dependent on the repetition of the coating process.

Disk-type samples were prepared using a cold press method at room temperature. FIG. 9 shows the bismuth telluride disk **90** fabricated with its nanocrystal powder. The nanoscale, nanovoid structure causes phonon scattering without disturbing electron mobility, thus increasing the figure of merit from low-dimensional nanocrystal Bi—Te materials.

The same or similar skills and/or techniques used to fabricate the nanovoid-imbedded Bi_2Te_3 ATE material described above can be readily extended to the fabrication of other nanovoid-embedded TE materials, such as cobalt antimonide (CoSb_3) and lead telluride (PbTe), for optimal thermoelectric performance at temperature ranges different from Bi_2Te_3 and SiGe. FIG. 3 shows several TE materials along with their associated best-suitable temperature ranges.

The present inventive energy conversion system is not limited to the above-noted layer materials. Other TE materials, and nanovoid embedded TE materials would also be suitable, and would be chosen based on the specific applications and temperature ranges. In general, suitable materials will have a high Seebeck coefficient, a high electrical conductivity and a low thermal conductivity.

In accordance with the present invention, these ATE materials can be utilized in the manufacturing of ATE energy conversion devices and systems, as illustrated in FIG. 10. To make a p-n junction for TE energy conversion, the TE matrix materials developed can undergo conventional doping processes to create N-type and P-type materials (i.e., semiconductors).

As understood in the art, “doping” refers to the process of intentionally introducing impurities into an intrinsic semiconductor in order to change its electrical properties. A P-type semiconductor is obtained by carrying out a process of doping wherein a certain type of atoms are added to the semiconductor in order to increase the number of free positive charge carriers. When the doping agent (acceptor material) is added, it accepts weakly-bound outer electrons from the semiconductor’s atoms, and creates holes (i.e., atoms that have lost an electron). The purpose of P-type doping is to create an abundance of such holes. When these holes move away from its associated negative-charged dopant ion, one proton in the atom at the hole’s original location is now “exposed” and no longer cancelled by an electron, resulting in a hole behaving as a quantity of positive charge. When a sufficiently large number of acceptor atoms are added, the holes greatly outnumber the thermally-excited electrons. Thus, the holes are the majority carriers in P-type materials, and the electrons are the minority carriers. In contrast, an N-type material is obtained by adding a doping agent known as a donor material, which donates weakly bound outer electrons to the semiconductor atoms. For example, an impurity of a valence-five element can be added to a valence-four semiconductor in order to increase the number of free mobile or carrier electrons in the material. These unbound electrons are only

weakly bound to the atoms and can be easily excited into the conduction band, without the formation of a “hole,” thus the number of electrons is an N-type material far exceeds the number of holes, and therefore the negatively charged electrons are the majority carriers and the holes are the minority carriers.

Non-limiting examples of doping material that could be used in the instant invention are boron and phosphor, which doping could be done in a known manner, such as by ion implantation or diffusion. In general, an array of pairs of p-n junction materials, or elements, is utilized to increase the thermal exposure area. As shown in FIG. 10, a TE module **100** can consist of three layers of p-n-junction arrays **102**, **103**, **104** in a tandem mode that operate most efficiently at high, medium, and low temperatures, correspondingly in a tandem mode, providing a cascaded conversion efficiency. In at least one advantageous embodiment, these TE layers **102**, **103**, **104** comprise advanced TE materials, making a cascaded efficiency greater than about 60 percent obtainable, as indicated in FIG. 11. While the shown embodiment consists of three layers, it should be understood that depending upon the desired application, the number of layers can be varied accordingly. Additionally, these layers can be assembled in the manner known in the art, for example, a metallized ceramic **105** could potentially be layered between them.

Such a tandem arrangement allows efficient energy harvesting from a heat source, thus allowing the present inventive energy conversion system to be effectively utilized in High Altitude Airship (HAA) applications where solar energy is considered as an energy source. In order to address the power-related requirements for lighter-than-air vehicles, including airships and hybrid fixed-wing configurations, the integration of the ATE devices can take on many different forms, dependent on configuration needs and mission requirements. As explained above, in general, an array of a pair of p-n junction materials is necessary to increase the thermal exposure area, and the ATE energy conversion device **100** may consist of multiple layers of p-n-junction arrays, as shown in FIG. 10. The first, or top, layer **102** is built from the array of thermoelectric material segments **101** that operate optimally at the higher temperatures, such as SiGe. The subsequent layers, or stages, are driven by the propagating thermal energy of the preceding layer. The selection of the appropriate thermoelectric material for each of these subsequent layers is chosen dependent on the optimal thermoelectric figure of merit, ZT, for the respective operating temperature ranges. Referring again to the general example as shown in FIG. 10, the second and third layers **103**, **104** of this 3-layer thermoelectric power system **100** are respectively built from PbTe and Bi_2Te_3 in a regenerative cycle mode of operation. Further, in at least one embodiment of the invention, it is desirable to utilize ATE materials such as nanovoid embedded Bi_2Te_3 and PbTe, and lattice-matched SeGi as the three layers. The invention, however, is not limited to these materials and may use only one or more layers of ATE materials.

In operation, the incident solar flux first heats up the initial layer **102** which is built with an optimized high temperature thermoelectric material. The unused thermal energy from the first layer is subsequently utilized by the second layer **103** which is built with an optimized mid-temperature thermoelectric material, such as PbTe. Repeating this process again, the third layer **104**, such as Bi_2Te_3 , uses the unused energy from the second layer to maximize the conversion of the energy that is otherwise underutilized. With this repeated process, the number of different thermoelectric material layers needed, also depends on the overall temperature range available and desired. With the available thermal energy from

the solar flux, the ATE can harness more energy than photovoltaic cells that use quantized electrons of the photons from the solar flux. The integration of advanced TE materials can provide significant levels of electrical energy because of this cascaded efficiency of multiple-layer TE modules **100** that are much higher than the efficiency of a single layer and the broad use of the solar thermal energy. The layered structure of the advanced TE materials is specifically engineered to provide maximum efficiency for the corresponding range of operational temperatures. A representative three layer system of advanced TE materials, as shown in FIG. **10**, generally operates at high, medium, and low temperatures, correspondingly in a tandem mode. The cascaded efficiency of such an arrangement is estimated to be greater than 60% as indicated in FIG. **11**. With multiple advanced thermoelectric material stages, a highly effective and efficient energy harvesting system may then be optimized for representative operational requirements such as maximum power, minimum weight, minimum size, etc.

As mentioned above, these ATE materials can be chosen to fit specific applications depending upon the overall temperature range available and desired. This same procedure can be used to construct specialized TE energy conversion devices in accordance with the present invention, for many different applications, including a variety of different heat sources. That is to say, by understanding each application prior to fabricating the inventive TE energy conversion device, the appropriate ATE materials can be chosen and layered (e.g. depending upon the original thermal load and a calculation of how much heat must be removed from this load by each layer, to achieve the desired performance objectives for each layer and overall).

Additionally, as would be known to one with ordinary skill in the art, the thickness of each layer can also be varied (for example, by increasing the number of sub-layers of the ATE material) until a desired temperature reduction is achieved prior to the thermal energy passing into the next layer, so that, optimally, when the energy is passed to the next layer it is at a temperature that will permit peak, or close to peak, thermal energy conversion performance by the receiving layer. Typically, a layer thickness might range from less than 1 mm to several millimeters, or more, in thickness, depending upon the material and application.

In this inventive fashion the overall efficiency of the system increases beyond that achieved by known methods (for example, where only one known TE material is used). Additionally, the ATE devices of the present invention become more effective than solar cells because the performance of solar cells is monolithically tied to band-gap energy structure, so that they only couple with certain spectral lines. Also, the higher the efficiency of the solar cells, the higher the cost and complexity of fabrication. For comparison purposes, FIG. **12** shows the layout of predicted figure of merits as a goal to achieve, which is added onto an existing diagram of solar cell efficiencies. As compared to solar cell technology in efficiency, the ATE system is competitive. However, considering the available energy from solar flux, the ATE system, using thermal energy, can harness more energy than photovoltaic cells that use the quantized electrons by photons from solar flux.

While solar energy conversion is discussed in detail herein, and specifically in reference to HAAs, it should be reiterated that the instant power conversion invention is not so limited in scope, rather the instant ATE energy conversion system can be used to harvest heat from a wide variety of sources (e.g., power plants, radioisotopes, automotive cooling systems, etc.) for many different energy generation and/or cooling

applications. Additionally, the completion of the fabrication of the final circuitry and fabrication of an operable thermoelectric conversion system using the inventive system disclosed herein, would be understood by someone with ordinary skill in the art as these techniques are well-known in the art.

There are several potential candidate energy harvesting technologies for HAAs, such as solar cells, fuel cells, Sterling engines, and TE generators. Due to the above-mentioned restrictions, ATE devices are extremely attractive because of the cascaded efficiency of the multi-layer TE modules of the present invention, that are much higher efficiency than the efficiency of a single layer and the broad use of solar thermal energy. As explained above, the layered structure of the ATE materials is specifically engineered to provide maximum efficiency for the corresponding range of operational temperatures. The present invention essentially functions like regenerative cycles in tandem. Such a highly effective energy harvesting feature of this tandem system based on multiple layers of advanced TE materials can be the basis of an HAA power budget plan.

In accordance with the present invention, to maximize the reception of solar thermal energy, an ellipsoid cross-sectioned high altitude airship (HAA) **135** has been designed, as shown in FIG. **13A**. In at least one embodiment, such an HAA can be 150 meters long, 60 meters wide, and 24 meters high. In size, this HAA is about 2.5 times larger than a Goodyear® blimp, which is 60 meters long. With this dimension of HAA **135**, the perpendicularly incident solar power amounts to about 9 MW. However, the daytime exposure varies with sun location. As shown in FIG. **16** (a cross-sectional view), if it is necessary, the HAA **135** can be reoriented to receive the maximum solar energy by keeping the top surface **135a** of the HAA **135** always substantially perpendicular to the solar angle **160**. In at least one embodiment, a vectored electric propulsion system can be used for this purpose.

When the top surface **135a** of HAA **135** follows the sun, the power management and control (PMC) station **141** installed under the belly of HAA **135** is designed to move on a guide rail **140** (shown in FIG. **14**), to reposition itself, always dangling at, or near, the bottom, or lowest point, of HAA **135** for every collector orientation. FIG. **16** shows the repositioned PMC **141** at the nadir point of HAA **135** along with the sun position **160**. In such a manner, the energy harvested from sun-rise to sun-set becomes effectively maximized, regardless of exposure variation over the course of the day. Using 20% efficient photovoltaic (PV) cells, the maximum converted power would be less than 2 MW. With the inventive advanced TE system of the same efficiency, the converted power would be greater than 4 MW because the cascaded efficiency of three layers is calculated to be approximately 49%. Considering a three-layered structure of the advanced TE materials having a FOM **5**, the cascaded efficiency amounts to be close to 66% (see FIG. **11**). If the amount of losses (35%) due to geometrical orientation (23%), reflection (7%), absorption (3%), and transmittance (2%) is considered for the estimation of cascaded efficiency, the total harvestable unit becomes 0.427 under the condition of 0.65Ω input instead of 1Ω used in FIG. **11**. Accordingly, the obtainable power amounts to be 3.84 MW which is substantial to accommodate several roles of the HAA. FIG. **13A** depicts some of the scenarios that might be feasible, such as feeding power to off-shore or isolated locations, for example, in lieu of having to build expensive power stations. The HAA can also become a mothership to wirelessly feed power to deployed unmanned vehicles.

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Referring to FIGS. 13, 15 and 17, in one embodiment of the present invention, the ATE power module 100 (FIG. 10) can be used in conjunction with linear parabolic troughs 130. These troughs 130 can have a 300 cm aperture width to collect solar power, as shown in FIG. 17. In at least one application, the back-surface 170 of ATE strips 100a is reflective to reduce solar energy absorption and faces outside directly to the cold environment of high altitude to drop the surface temperature by convective cooling. The temperature at 70,000 feet or above in the atmosphere is extremely cold and hovers below -73° C. Accordingly, to maximize the performance of the ATE system, the solar trough concentrators are used to focus solar flux to the surface 171 of the 1st layer that faces the reflector trough 130 while the back side 170 of the 3rd layer faces the cold atmosphere to increase the temperature gradient. In at least one embodiment, the material of the reflector trough 130 can be, for example, enhanced aluminum coated thin-film membrane which is sufficiently hardened to maintain its parabolic shape. Each reflector 130 can be covered by a transparent membrane 151 that allows sun light to impinge into the parabolic trough 130. The strip of ATE power module 100a is located on a focal line of the parabolic trough 130 and connected to the transparent thin film window material 151, for example, both edges of the strip 100a can be connected to the transparent material 151. An additional advantage of this type of ATE energy conversion system is that the structural formation of such solar trough 130 will enhance the strength of large sized HAA.

The nighttime power requirements of HAAs may not be alleviated because the HAA's nighttime operation frequently has the same importance as their daytime operation. Therefore, the power for nighttime operation typically must be the same level as that of the daytime usage. Based on the daytime figure for required power, three components of power infrastructure are actively involved to supply necessary power. That is to say, for nighttime, the power required can be augmented from the onboard fuel cells, battery and a rectenna array 180a that is attached at the bottom surface 135b of HAA 135 (see FIGS. 14 and 15, where the rectenna array is indicated by a dashed line). These combined systems provide at least a megawatt level of power for the intermittent operation.

Hydrogen fuel-cells with the capacity of several hundreds kilo-watt level are onboard for the nighttime power generation. The water which is an end product of fuel-cell process is collected and dissociated into hydrogen and oxygen through electrolysis process using the power harvested during daytime. The hydrogen and oxygen is collected and fed back to fuel cells later at nighttime.

The power stored in the thin-film battery during daytime can be drained out for nighttime use. The battery storage capacity (~600 Coulomb/gram) is proportional to its own weight increase. Therefore, the battery is not regarded as the major power provider for night time use. It can be used for emergency purposes.

The arrays of thin-film rectennas 180, as shown in FIG. 18A, can be readily fabricated on a flexible film 181 which can be used within the structural envelope of the HAA. In at least one embodiment, the arrays 180/180a are patched under the bottom surface 135b of HAA 135 (see FIG. 15, which depicts a cross-sectional view of the HAA shown in FIG. 14), to receive and convert microwave power 152 into DC Power, as illustrated schematically in FIG. 18B. The conversion efficiency of rectennas is unusually high (~85%), but the collection efficiency is poor because of the dispersive nature of microwave. The bottom surface area of HAA 135 is wide and nearly flat to enable the HAA 135 to collect most of dispersed microwave energy. At the 21 km (~70,000 ft) altitude, the area

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required to collect the W-band (90–100 GHz) microwave is approximately 48 meters in diameter. This number is calculated by the Gaubau relationship, which is defined by the following formula:

$$\tau = \frac{\sqrt{A_r \cdot A_t}}{\lambda Z}$$

wherein: A_r is the area of receiving antenna; A_t is the area of transmitting antenna; Z is the distance between the transmitting and receiving antennas; λ is the wavelength of microwave; and τ is the parameter determined for 100% reception which, in the case for microwaves, is 3.

In at least one embodiment of the present invention, the bottom surface 135b of HAA 135 can be 150 meters long and 60 meters wide. Accordingly, the microwave power at the W-band can be delivered to the array of rectennas 180a at the bottom surface 135b of HAA 135 almost all without loss. FIG. 19 shows a logic diagram of microwave power use. The power 191 received by rectenna arrays 180a is allocated and distributed by the power allocation and distribution (PAD) logic circuit 192 to specific nodal points where the power is mostly needed, such as propulsion unit or subsystems 193. Otherwise, the excessive power can be stored in an array of thin-film solid-state batteries 194 for later use. Thus, a large amount of microwave power can be delivered to the HAA 135 from a ground or a ship-board microwave power beaming station. Even for a remotely dispatched HAA 135, wireless airborne electro-refueling by airplanes is possible. Multiple microwave stations combined can aim their beams onto a rectenna-equipped HAA 135 to feed the power required for the operation at night.

The power harvested by the inventive ATE generator can be utilized for the power transmission to UAVs, for onboard systems operation, and for internal power requirements such as propulsion and control. FIG. 13A illustrates a graphical scenario of operational mode of an HAA 135. If more power is required, of course, in at least one embodiment, it is solved by the enlargement of HAA 135, and the utilized ATE system 100a with troughs 130. The total power harvested (3.84 MW) can be distributed for propulsion for stationary positioning and maneuvering, power storage, microwave beaming for MAV or UAV operations, laser power beaming to ground locations, such as for illumination or telecommunication purposes, and house-keeping activities. Such applications require a continuous power source that will run for several hours in a sequential or a pulse mode anytime throughout the day and the night. FIG. 20 shows the power flow diagram based on the power estimation that is to be harvested by the ATE array placed on top of the HAA. The power allocated for the operations of those onboard devices is estimated to give a glimpse at one possible power picture.

The power harvested by the inventive ATE generator can also be utilized for propulsion for position correction and maneuver. The wind at an altitude of 21 km (70,000 feet) or above is substantially lower than typical seasonal jet-streams that exist within the northern hemisphere. Nevertheless, the large cross-section of the HAA is vulnerable to drifting along with wind. Continuous positioning and maneuvering operation of the HAA against the wind is necessary and crucial for the stationary operation and maximum solar exposure over solar angle variation. Otherwise, the HAA will drift away to an undesirable location where the use of onboard devices may be impossible. The propulsion for position correction and maneuvering is also required during the night time.

Another potential embodiment of the inventive HAA configuration includes a base for UAV or MAV airships. A novel lightweight, high performance, long endurance UAV configuration, as shown in FIG. 21, has been developed that combines a polymer structure with an electrical power generating system to produce new missions and capabilities for air vehicles. As presently envisioned, this class of UAV satisfies aeronautical missions for high altitude, characterized by long endurance, electric propulsion, propellantless, and emissionless. The configuration utilizes a polyimide structural material for creating the primary wing and fuselage elements of the vehicle. The polymer structure functions to carry normal, bending, and pressure loads as experienced from sea-level to cruising altitudes. The polymer structure incorporates arrays of rectennas **180b** to form a wireless power generation system. The rectenna system **180b** has been demonstrated at microwave wavelengths (X-Band) to provide 275 volts from 18 milli-Watts of incident energy. The rectenna system **180b** can be designed for other and higher frequencies depending on configuration requirements, atmospheric transmissibility, etc. The resulting electrical energy can be used as power for electrical motors for propulsion of the UAV's alone, in combination with electrical storage systems, or in combination with other hydrocarbon engines, including hybrid modes of operation.

As conceived, the UAV is air-launched from and returned to the HAA base. The HAA base for UAVs is built under the HAA, as shown in FIGS. 14 and 15. The UAVs may also be launched or retrieved by hand, machine, towing, or dropped from other aircraft and/or helicopters. By nature of the structural material and concept of utilization, the UAV does not require landing gear or skids. As such, the structural design requirements for takeoff, landing, and taxiing are reduced or eliminated and thereby relax the overall structural design loads and requirements.

To sustain a long duration operation, the helium or helium/hydrogen mixture filled fat-body airframe of UAVs is considered to reduce the power requirement for propulsion by both reducing the body weight and increasing the lift force by buoyancy. The fat-body framed UAV mode **210** to be propelled by electric motors is shown in FIG. 21. Two electric motor driven propellers **211**, **212** are located at both the wing-tips and control the flight direction by changing rotational speed. The power for these planes is obtained from microwave through rectenna arrays **180b** that are integrated on the skin of the airframe. The range of maneuver is determined by the envelope of microwave beaming column and the guided direction of beam. As long as any MAVs or UAVs are within the beam column, the power is continuously fed into them.

Suppose that a UAV has a 10 m^2 rectenna arrays that are integrated into the skin of fuselage and both wings as shown FIG. 21. If 1 MW of microwave power as described in the block diagram of FIG. 20 is transmitted at w-band, the power flux density of microwave at the ground level will be approximately 60 mW/cm^2 . The power received by a UAV which is a 20 km away to the ground level and has a 10 m^2 rectenna arrays will amount to be 6 kW within the power beam column of 50 meters in diameter. Using the same logic shown in FIG. 19, the power is allocated to the propulsion system and other functional systems, such as probes. Suppose that the maneuver of the UAV requires 4 kW of the received power. The rest can be used for sensors and probes for other operations. However, the power receiving area of MAVs or UAVs is limited due to their own limited sizes. Therefore, they require an extra lifting force to stay aloft. The helium-filled MAV or UAV **210** as shown in FIG. 21 will gain an extra lifting force.

The UAV size of 5 m^3 helium filled will gain the buoyancy force of 51 N which will reduce the weight by approximately 5 kg.

Another scenario for HAA use is for laser power transmission technologies for space applications which were developed in late 1970 through the 1980's using the directly solar pumped iodine laser and also a high power diode laser array. The efficiencies of continuous wave (CW) lasers are, in general, poor, especially for the short wavelength lasers. If we consider a laser with 10% efficiency, the actual laser power to be conveyed through the beam becomes 100 kW level. With a pulse forming network, the laser power output would be much higher to a few tera-watts (TW) level by pulse compression. The reflectors **220** that are installed on a HAA can also be used to relay the laser beam power **221** to selected locations through the relay satellite **222** as shown in FIG. 22. However, if the HAA has sufficient power available from utilization of the ATE conversion device of the present invention, the relay station would not be necessary. Additionally, energy harvested by the ATE device **100/100a** can also be used for internal power requirements of the HAA. The internal power requirement is determined from the power consumption by the PMC station movement over the guide rail, communication equipment, and system monitoring devices. Additionally, onboard radar systems can also be operated with this energy. The onboard radar operation can be used for monitoring any flying objects or ground or sea level activities of interest.

The new concept HAA, as described above, has an elliptical cross-section perpendicular to the thrust axis to expand the solar exposure area, unlike the conventional airships with a circular cross-section. FIG. 13B shows the elliptical cross section of an embodiment of the airship. Accordingly, the overall shape of the new concept airship is flattened as illustrated in FIGS. 13A and 15. Although the elliptical cross-section **131** of the airship **135** may be structurally less sturdy or slightly heavier than the circular cross-section, the benefits of the elliptical shape are greater in consideration of the lift force and the stability of flight that might compensate the shortcomings of elliptical cross-section. If the structural reinforcement of the elliptical cross section should be required to maintain the same strength level of a circular cross sectioned, the weight increase due to the elliptical cross section of airship would be less than 20%. The near flat-top surface **135a** of the airship **135** offers a wide area to accommodate a energy harvesting device from sun light, such as solar cells or the advanced thermoelectric generators of the present invention. As shown in FIG. 14, the HAA can have guide rail systems **140/146** to locate the PMC station **141** and the UAV hangers **142** to the nadir position of HAA **135**. The purpose of rotational capability along the guide rail **140** is to maximize the incidence of solar flux by setting the top surface of HAA **135** always perpendicular to sun light **160**. Whenever the PMC station **141** moves on the guide rail **140**, the HAA rotates the PMC station **141** and sets the PMC station **141** at the lowest level as shown in FIGS. 14 and 16 since the PMC station **141** is typically the heaviest unit of the HAA. Movement of PMC **141** on guide rail **140** can be accomplished through conventional means (e.g. computer controlled and electric motor driven). Similarly, in at least one embodiment, guide rails **146** can be provided, to move the UAV hangars **142** in the same manner as the PMC station **141**.

Although the invention has been described relative to specific embodiments thereof, there are numerous variations and modifications that will be readily apparent to those skilled in the art in light of the above teachings. It is therefore to be

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understood that, with in the scope of the appended claims, the invention may be practiced other than as specifically described herein.

What is claimed is:

1. A method for forming high figure of merit thermoelectric materials, comprising:
 - providing nanocrystals of bismuth and tellurium;
 - preparing a void generator material including a plurality of nanoparticles each having a metallic outer coating, wherein the void generator material is ferritin protein;
 - preparing a solution mixture of the bismuth nanocrystals, tellurium nanocrystals and the void generator material;
 - depositing the solution mixture onto a substrate;
 - heating the deposited solution mixture in an oxygen environment to create a plurality of nanovoid structures from the nanoparticles resulting in a nanovoid incorporated bismuth-tellurium film;
 - following the heating, treating the film to remove any oxygen components remaining from heating the mixture in the oxygen environment; and
 - causing the formation of a crystalline structure in the film.
2. The method of claim 1, wherein the metallic outer coating of the nanoparticles is selected from the group consisting of gold, cobalt, platinum, manganese, and iron.
3. The method of claim 1, wherein the metallic outer coating of the nanoparticles is in the range of 3 to 4 nm thick.
4. The method of claim 1, wherein the nanoparticles are generally spherical in shape.
5. The method of claim 1, wherein the nanoparticles have an inner diameter of 8 nm and an outer diameter of 12 nm.
6. The method of claim 1, wherein the substrate is silicon.
7. The method of claim 1, wherein the solution mixture is deposited on the substrate by a method selected from the group consisting of spin-coating, dipping, and solvent casting.
8. The method of claim 1, wherein the oxygen environment is 99.999% pure oxygen.
9. The method of claim 1 wherein the deposited solution mixture is heated to no more than 400° C.
10. The method of claim 1 wherein the deposited solution mixture is heated for approximately 1 hour.
11. The method of claim 1, wherein the film is treated to remove any oxygen components remaining from heating the mixture in the oxygen environment and formation of a crystalline structure in the film are accomplished by performing hydrogen calcination and hydrogen plasma quenching.

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12. A method for forming high figure of merit thermoelectric materials, comprising:
 - providing nanocrystals of bismuth and tellurium;
 - preparing a void generator material including a plurality of nanoparticles each having a metallic outer coating;
 - preparing a solution mixture of the bismuth nanocrystals, tellurium nanocrystals and the void generator material;
 - depositing the solution mixture onto a substrate;
 - heating the deposited solution mixture in an oxygen environment to create a plurality of nanovoid structures from the nanoparticles resulting in a nanovoid incorporated bismuth-tellurium film;
 - following the heating, treating the film to remove any oxygen components remaining from heating the mixture in the oxygen environment; and
 - causing the formation of a crystalline structure in the film, wherein the film treatment and formation of a crystalline structure in the film are accomplished by performing hydrogen calcination and hydrogen plasma quenching.
13. The method of claim 12, wherein the void generator material is an organic material.
14. The method of claim 12, wherein the void generator material is ferritin protein.
15. The method of claim 12, wherein the metallic outer coating of the nanoparticles is selected from the group consisting of gold, cobalt, platinum, manganese, and iron.
16. The method of claim 12, wherein the metallic outer coating of the nanoparticles is in the range of 3 to 4 nm thick.
17. The method of claim 12, wherein the nanoparticles are generally spherical in shape.
18. The method of claim 12, wherein the nanoparticles have an inner diameter of 8 nm and an outer diameter of 12 nm.
19. The method of claim 12, wherein the substrate is silicon.
20. The method of claim 12, wherein the solution mixture is deposited on the substrate by a method selected from the group consisting of spin-coating, dipping, and solvent casting.
21. The method of claim 12, wherein the oxygen environment is 99.999% pure oxygen.
22. The method of claim 12 wherein the deposited solution mixture is heated to no more than 400° C.
23. The method of claim 12 wherein the deposited solution mixture is heated for approximately 1 hour.

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